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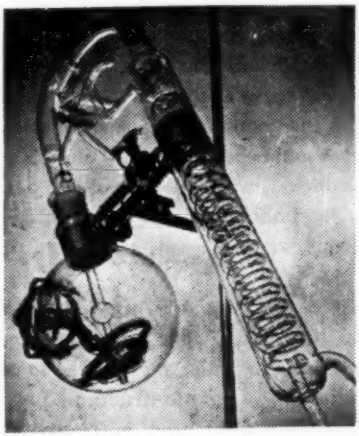

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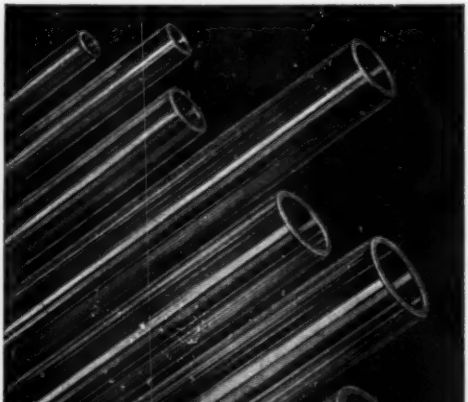

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[Jour. Indian Chem. Soc., Vol. 35, No. 1, 1958]

SOME APPLICATIONS OF RANEY NICKEL TO SYNTHETICAL AND CONSTITUTIONAL PROBLEMS*

By K. Venkataraman

Among the most widely used reduction catalysts is nickel, prepared according to Raney[1] by treating a nickel-aluminium alloy with warm caustic soda solution to dissolve the aluminium. Raney nickel of various grades of activity can be prepared by altering the mode of addition of the alloy, the concentration of the alkaline solution, the temperature and time of digestion, and the intensity of the washing process. These factors were studied in detail by Adkins[2], who classified the catalysts as W-1, W-2, etc., and standardized their activity in terms of the time and temperature for the reduction of β-naphthol to the two tetrahydro derivatives and the yields of the *ac* and *ar* isomers. The activity of Raney nickel is increased by adding to the alloy in portions caustic soda solution instead of the usual reverse procedure; this catalyst reduces *cyclo*hexanone in ethanol to *cyclo*hexanol at 25° and atmospheric pressure in 22 minutes, while the W-7 catalyst requires 40 50 minutes[3].

Raney-nickel reduction may be effected under a wide variety of conditions of temperature, pressure and quantity of catalyst. External hydrogen at pressures varying from atmospheric to 200 atmospheres has been used. Instead of hydrogen itself, hydrazine and other compounds which liberate hydrogen in the presence of the catalyst can be employed[4]. Nitro compounds in alcoholic solution are reduced to amines in good yields by Raney nickel and hydrazine hydrate; by varying the concentration of hydrazine, azoxybenzene and hydrazobenzene can be obtained[5]. Using Raney nickel as a hydrogen transfer agent, reductions have been carried out with the aid of hydrogen donors such as *cyclo*hexanol, as well as oxidations in the presence of hydrogen acceptors such as *cyclo*hexanone; thus benzoin was reduced to dibenzyl or oxidized to benzil[6]. The reported reduction[6] of 9-anthraldehyde by this method to 9-hydroxymethylanthracene and anthracene needs confirmation because of the susceptibility of the anthracene nucleus to reduction.

Raney-nickel Reduction without External Hydrogen

The ability of Raney nickel to effect reductions (e. g., of ethylenic bonds) in the absence of external hydrogen, utilising the adsorbed hydrogen, was demonstrated by Bougault, Cattelain and Chabrier[7]. They were also the first to show that Raney nickel was valuable as a reagent for the removal of sulphur; thus thioglycollic acid was reduced to acetic acid. The fission of a carbon-carbon bond was found by Snyder and Cannon[8] to accompany the desulphurization of ethers of ethylenedithiol, methane being formed in addition to ethane.

* Acharya Prafulla Chandra Ray Memorial Lecture delivered at the National Chemical Laboratory, Poona, on August 2nd, 1957 under the auspices of the Indian Chemical Society.

The Mozingo Method

Mozingo and his collaborators studied the action of Raney nickel on representative sulphur compounds, such as sulphides, sulphoxides, sulphones and sulphur-containing heterocyclic compounds in view of contemplated investigations of the structure of natural products containing sulphur. Biotin methyl ester was desulphurized by Raney nickel to desthiobiotin methyl ester, hydrolysis of which led to 7:8-diaminopelargonic acid, from which the structure of biotin was deduced[9]. By the action of Raney nickel on an aqueous solution of the sodium salt benzylpenicillin yielded desthiobenzylpenicillin in which the β-lactam ring remained intact; further reduction broke the carbon nitrogen bond of the β-lactam ring and gave *N*-phenylacetyl-L(+)-alanyl-D(−)-valine. This degradation of penicillin was of great importance since it provided direct evidence for the presence of the β-lactam ring[10].

Reduction or hydrogenolysis by treatment with massive amounts of Raney nickel catalyst in a solvent such as boiling ethanol without the addition of hydrogen has been extensively investigated by Mozingo and his collaborators, and the procedure is therefore referred to in the sequel as the Mozingo method[11].

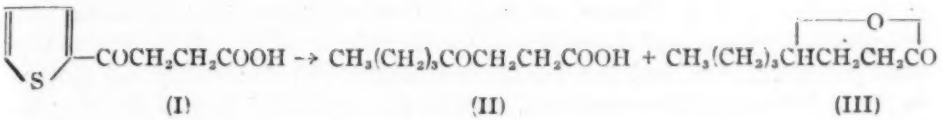
The Schwenk-Papa Method

Whitman, Wintersteiner and Schwenk[12] reduced oestrone to oestradiol (α and β) by treatment with boiling caustic soda solution and Raney (nickel-aluminium) alloy. This technique, which may be termed the Schwenk-Papa method[13], involves the action of nickel catalyst and hydrogen, both obtained *in situ*[13]. The following are some of the reductions which were effected under these conditions.

Oleic acid	→	Stearic acid
$Ph(CH_2)_xCOR$	→	$Ph(CH_2)_x$-CHOH-R ($x=1$ or more)
m-Chlorobenzoic acid	→	Benzoic acid
p-Chlorobenzaldehyde	→	Toluene
Sulphobenzoic acids	→	Benzoic acid
β-(α-Furyl)acrylic acid	→	β-Tetrahydrofurfurylpropionic acid + γ-*n*-propylbutyrolactone.

An alkoxyl group, *o*- or *p*- to a *m*-directing group, was replaced by hydrogen; a *m*-alkoxyl was unaffected. Thus *o*- and *p*-methoxybenzoic acids gave a quantitative yield of benzoic acid, and *p*-nitroanisole gave a mixture of aniline (20%) and *p*-anisidine (70%).

Papa, Schwenk and Ginsberg[14] found that β-(α-thenoyl)propionic acid (I) on treatment with Raney alloy in aqueous caustic soda yielded a mixture of about equal parts of γ-ketocaprylic acid (II) and γ-caprylolactone (III), or only (III), depending on the ratio of alloy and the reaction time. The higher homologue, ω-(α-thenoyl)pelargonic acid (IV) gave only 10-hydroxymyristic acid (V). Thionaphthenequinone yielded mandelic acid.



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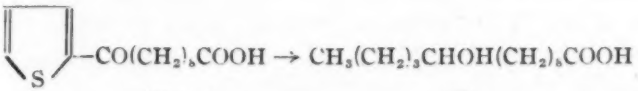


(IV) (V)

In view of the work of Mozingo, Schwenk and others, apart from the work carried out in my laboratory[15-21], it is remarkable that Badger, Rodda and Sarse[22], who have prepared long-chain fatty acids by the Raney-nickel desulphurization of alkylthienylbutyric acids, have made the statement that "the potentialities of desulphurization as a synthetic method seem to have been largely unrecognized." Similar applications of Raney-nickel desulphurization have also been made by Grey *et al.*[23], Buu-Hoi *et al.*[24], and Wynberg and Logothetis[25]. Naphthalene and phenanthrene derivatives have been synthesized by Raney-nickel desulphurization of appropriate thiophene derivatives[26].

Three modifications of Raney nickel were examined by Hurd and Rudner[27] in the desulphurization of compounds containing the thiocarbonyl group, thiazoles and thiophenes. Some of the reductions were: *o*-tolylthiourea → *o*-toluidine; thiobenzanilide → benzylaniline; 2-mercaptobenzothiazole → aniline + small amounts of *o*-aminothiophenol and benzothiazole; 2-mercapto-4-phenylthiazole → acetophenone; 2-mercapto-4-hydroxythiazole → acetaldehyde; 2-acetylthiophene → 2-hexanone + small amounts of acetaldehyde and ethanol.

Among other applications of Raney-nickel desulphurization to reactions useful in synthesis may be mentioned the conversion of CO to CH_2 via the thioacetals (diethylmercaptals[28]; the reduction of phenanthridone to phenanthridine via the thione[28a]; the conversion of cyanuric chloride to *s*-triazine via the *tris*methylmercapto compound[29]; the reduction of thioamides to amines[30] and to aldehydes[31]; and the conversion of 5-phenyl-2:4-dithiohydantoin into 4-phenylglyoxaline[32].

When aromatic mercaptals are treated with Raney nickel from which hydrogen has not been completely removed, binuclear hydrocarbons, such as diphenyl and dibenzyl, are formed[33].

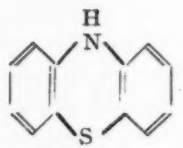
Raney-nickel desulphurization can be effected without change in an asymmetric centre situated at a distance from the sulphur atom[34]. The enantiomorphic 2-phenyl-2-phenylmercaptopropionamides give racemic 2-phenylpropionamide, but the corresponding sulphones give optically active 2-phenylpropionamides. The two desulphurizations therefore proceed by different mechanisms[35]. Raney-nickel reduction of 2-methoxy-2-phenylpropionic ester to 2-phenylpropionic ester proceeds with predominant configurational retention, but is not completely stereospecific[36,37].

During the course of our studies on the constitution of sulphur dyes, sulphurised vat dyes, thioindigoid dyes and dyes containing sulphonic groups, and in the light

of the earlier work of Mozingo, Schwenk and others, Raney-nickel reductions and desulphurizations appeared to provide a useful mode of attack. In a preliminary investigation[15], it was found that J-acid on treatment with Raney alloy and aqueous caustic soda gave 6-amino-1-naphthol, indicating a method of preparation of relatively inaccessible naphthalene derivatives from readily available dye intermediates; β-naphthol gave a mixture of the *ac* and *ar* tetrahydro compounds; Naphthol AS gave 5:6:7:8-tetrahydro-2-hydroxy-3-naphthanilide; and carbazole under Mozingo conditions (Raney nickel in boiling ethanol) gave tetrahydrocarbazole.

N-*Alkylation*

Thiodiphenylamine (VI) on treatment with Raney nickel in boiling ethanol gave diphenylamine; with benzidine-sulphone (VII) desulphurization was accompanied by *N*-alkylation, yielding *N*:*N*′-diethylbenzidine (VIII)[15]— a reaction of considerable interest which was subsequently submitted to a more detailed study as a general method of *N*-alkylation[38]. Rice and Kohn have described the preparation of *N*:*N*′-diethylbenzidine by this method[39]. Mozingo had shown earlier that the action of Raney nickel and boiling ethanol on nitrobenzene, azobenzene and hydrazobenzene led to *N*-ethylaniline[11].



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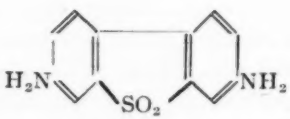
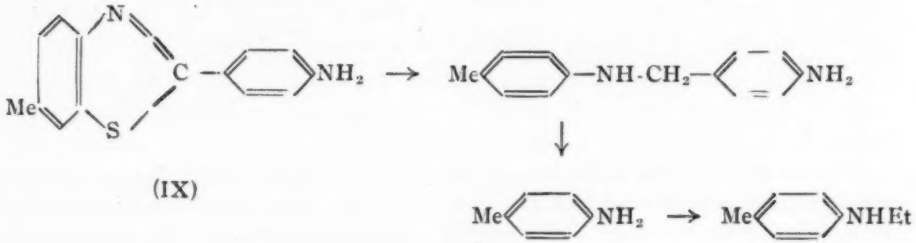


(VII)

(VIII)

Dehydrothio-*p*-toluidine (IX) in ethanol was degraded by Raney nickel at room temperature; *N*-ethyl-*p*-toluidine was obtained in nearly 90% yield, apparently by the following mechanism as shown by the fact that benzylaniline gave *N*-ethylaniline.



(IX)

When equal parts of *p*-toluidine and Raney nickel were refluxed with ethanol, no unreacted *p*-toluidine was detectable after two hours; the sole product was *N*-ethyl-*p*-toluidine (88% yield), and a characteristic feature of the new procedure for *N*-alkylation was that no tertiary amine was formed, and there was no problem of separation of secondary from primary and tertiary amines. It was possible to carry out the reaction at room temperature, but it then required 18 hours to complete.

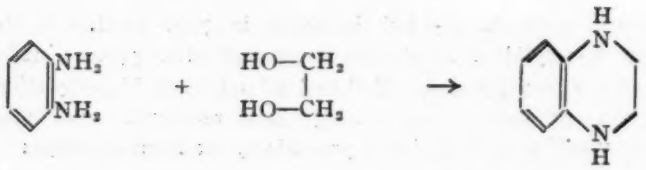
p-Aminobenzoic acid gave the *N*-ethyl derivative in 70% yield. A steric effect was noticed with *m*-2-xylidine which was unaffected after 54 hours' refluxing with ethanol in presence of Raney nickel. Methanol did not effect *N*-methylation of aniline or *p*-toluidine, the primary amine having been recovered unchanged. These results support the view[40] that *N*-alkylation proceeds by the following steps:

$$RCH_2OH \xrightarrow{-H_2} RCHO \xrightarrow{ArNH_2} ArN = CHR \longrightarrow ArNHCH_2R.$$

n-Propanol, *n*-hexanol and *n*-dodecanol yielded the corresponding secondary amines, but the higher alcohols required progressively longer periods of treatment. *iso*Propanol also reacted with *p*-toluidine to form *N-iso*propyl-*p*-toluidine (48% yield), but prolonged treatment (24 hours) was necessary. With *cyclo*hexanol and *p*-toluidine, the interesting observation was made that the expected *N-cyclo*hexyl-*p*-toluidine was accompanied by 4-methyldi*cyclo*hexylamine, although the reduction of the benzene nucleus by Raney nickel under such mild conditions was not anticipated. A similar result was obtained with aniline and *cyclo*hexanol, the products being *N-cyclo*hexylaniline and di*cyclo*hexylamine[38].

Alkylation of primary alkylamines was next studied. When *n*-butylamine was treated with Raney nickel in boiling ethanol, no primary amine could be detected after 4 hours. The reaction mixture gave *N*-ethyl-*n*-butylamine and di-*n*-butylamine, together with a very small amount of a product which appeared to be diethylbutylamine. When the reaction was carried out at room temperature for 20 hours, *N*-ethyl-*n*-butylamine and di-*n*-butylamine were again formed. The formation of di-*n*-butylamine in these experiments indicated that in the presence of Raney nickel two molecules of *n*-butylamine reacted with each other. When *n*-butylamine itself was treated with Raney nickel in aqueous solution on a water-bath, di-*n*-butylamine and tri-*n*-butylamine were formed.

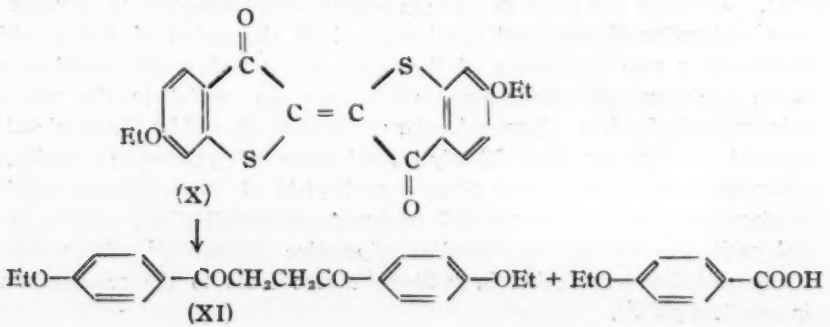
When *o*-phenylenediamine was treated with Raney nickel in ethyleneglycol on a boiling water-bath under stirring, the amine could not be detected in the reaction mixture after 14 hours. 1:2:3:4-Tetrahydroquinoxaline was isolated in low yield, together with a liquid containing nitrogen and oxygen which remained to be identified. Although the yield of 1:2:3:4-tetrahydroquinoxaline is low, its synthesis from *o*-phenylenediamine and ethyleneglycol by the action of Raney nickel is of interest as a new application of Raney nickel in organic synthesis and as a new route to 1:2:3:4-tetrahydroquinoxaline, which may be useful in the preparation of quinoxaline derivatives. Intramolecular cyclizations effected by Raney nickel have been reported by other workers. Catalytic cyclization of 5-amino-2:2:5-trimethyl-3-aza-1-hexanol with Raney nickel gives a 79% yield of 2:2:5:5-tetramethyl-2:3:4:5-tetrahydropyrazine[41]. Raney-nickel treatment of $RN(CH_2CN)_2$ results in reduction and cyclization to the corresponding piperazine derivative[42]. Dehydrogenation by Raney nickel of an 1:4-diol in boiling benzene leads to the corresponding lactone in excellent yield[43].



After our work was completed, Rice and Kohn[44] and Ainsworth[45] reported the *N*-alkylation of primary aromatic amines with alcohols and Raney nickel. Rice and Kohn carried out the reaction for longer periods and Ainsworth used larger amounts of Raney nickel. From β-naphthylamine and ethanol Ainsworth obtained only *N*-ethyl-β-naphthylamine, but our experience with naphthalene derivatives has shown that partial hydrogenation of the naphthalene nucleus is difficult to avoid. Rice and Kohn failed to effect *N*-alkylation by *iso*propanol, but Ainsworth confirmed our observation that prolonged heating resulted in the formation of *N*-*iso*propylaniline in about 50% yield. Ainsworth found that the reaction of Raney nickel and alcohols with primary aliphatic amines was more complex; 2-phenylethylamine and ethanol gave di-(2-phenylethyl)amine, and benzylamine gave dibenzylamine.

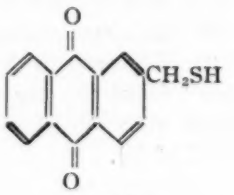
Desulphurization of Thioindigoid Dyes

The action of Raney alloy and aqueous caustic soda at about 100° on thioindigo and its derivatives has led to a new method for the synthesis of diphenacyls, which are otherwise not easy to prepare and which are useful intermediates for cyclization to 2:5-diaryl-furans, pyrroles and thiophenes[16-17]. Thioindigo itself gave only a 12% yield of diphenacyl, other products being 1:4-diphenylbutane and benzoic acid; but 6:6′-diethoxythioindigo (X) gave 4:4′-diethoxydiphenacyl (XI) in 80% yield, together with a small amount of *p*-ethoxybenzoic acid. As mentioned earlier, ketones of the type ArCOR yield the hydrocarbon $ArCH_2R$ under the Schwenk-Papa conditions of reduction, and the isolation of diphenacyls from thioindigoid dyes must be explained by poisoning of the nickel catalyst by sulphur after desulphurization has taken place, resulting in the diphenacyls not undergoing further reduction. Since benzoic acids were among the reaction products, the action of Raney alloy and boiling caustic soda solution on acetophenone was examined; benzoic acid was produced. The mechanism by which acetophenone is converted into benzoic acid needs to be investigated.

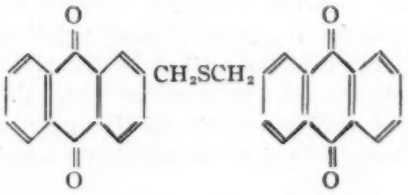


Action of Raney Nickel on Anthraquinone Derivatives

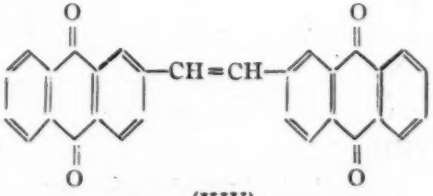
In connection with work on the constitution of dyes, such as Cibanone Yellow R and Orange R, obtained by the thionation of anthraquinone derivatives[46,47], the action of Raney alloy and caustic soda solution on anthraquinone, 2-methylanthraquinone, 2-mercaptomethylanthraquinone (XII), *bis*-2-anthraquinonylmethyl sulphide (XIII) and the corresponding disulphide was studied[18]. Anthraquinone gave 1:2:3:4-tetrahydroanthraquinone. When 2-methylanthraquinone was reduced with varying amounts of Raney alloy, several hydrogenation products of 2-methylanthraquinone were obtained. One was 1:2:3:4-tetrahydro-6-methylanthraquinone, the constitution of which was proved by oxidation to adipic and 4-methylphthalic acids. Desulphurization of (XII) gave 2-methylanthraquinone, 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid; (XIII) gave 2-methylanthraquinone and traces of anthraflavone (XIV); and the disulphide gave 2-methylanthraquinone, 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid. Anthraflavone gave decahydroanthraflavone as the major product and a small amount of 1:2:3:4-tetrahydro-6-methylanthraquinone, the latter being formed by fission of the ethylenic bond.



(XII)



(XIII)



(XIV)

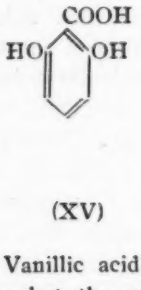
Synthesis of γ-Resorcylic Acid

In 1949 Kenner and Murray[48] described an interesting method for the reduction of phenol to benzene via the tosylate (*p*-toluenesulphonate), which underwent hydrogenolysis when an alcoholic solution was treated with Raney nickel and hydrogen at atmospheric pressure and room temperture:

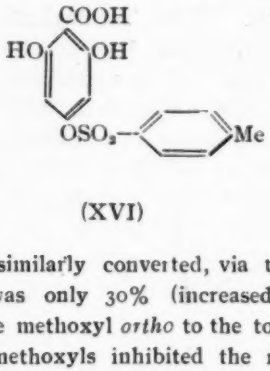
$$2Ph{-}O{-}SO_2C_7H_7 + Ni + H_2 \rightarrow 2C_6H_6 + Ni(OSO_2C_7H_7)_2.$$

m-Acetamidophenol was thus reduced to acetanilide (90%), and methyl salicylate to methyl benzoate (80%); β-naphthol led to tetralin, the naphthalene ring undergoing further hydrogenation. We have used the Kenner-Murray reduction for a variety of

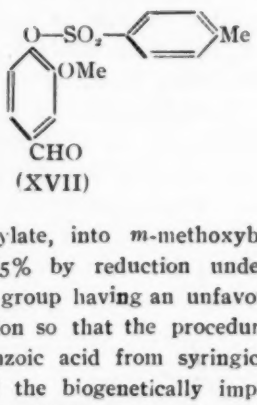
synthetical purposes. It provided, for instance, a new and convenient route to γ-resorcylic acid (XV), in the sodium salt of which there was a passing interest as a therapeutic agent in rheumatic fever for which advantages were claimed in comparison with sodium salicylate; (XV) was prepared in an overall yield of about 75% from phloroglucinol by carboxylation, mono-*O*-tosylation to form (XVI), and final hydrogenolysis of the potassium salt under the Murray-Kenner conditions.



(XV)



(XVI)



(XVII)

Vanillic acid was similarly converted, via the tosylate, into *m*-methoxybenzoic acid; but the yield was only 30% (increased to 65% by reduction under the Mozingo conditions), the methoxyl *ortho* to the tosylate group having an unfavourable effect. Two adjacent methoxyls inhibited the reduction so that the procedure was not available for the preparation of 3:5-dimethoxybenzoic acid from syringic acid. Seshadri[49] has used the method for the preparation of the biogenetically important 6 methylsalicylic acid from orsellinic acid. V. Ramanathan[50] found that the Mozingo reduction of vanillin tosylate (XVII) gave *m*-cresylmethyl ether (60%), while the Murray-Kenner reduction gave *m*-methoxybenzyl alcohol (80% yield).

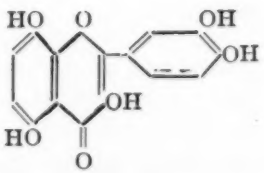
(XVIII) (XX)

Synthesis of 5-Hydroxyflavones

Removal of a phenolic hydroxyl group by hydrogenolysis of the tosylate has proved to be useful in the flavone and xanthone series[20, 50]. Chrysin (5:7-dihydroxyflavone) has been converted into 5-hydroxyflavone, and galangin-3-methyl ether (5:7-dihydroxy-3-methoxyflavone) to 5-hydroxy-3-methoxyflavone. A general method has thus become available for the synthesis of 5-hydroxyflavones, which are of interest because of their possible occurrence in nature and also as intermediates for the synthesis of naturally occurring 5:8-dihydroxyflavones by the Elbs-Seshadri persulphate oxidation. Chrysin and galangin-3-methyl ether readily gave the 7-tosyl ester (XVIII) and (XIX) on treatment with a molar proportion of tosyl chloride and excess of anhydrous potassium carbonate in boiling acetone. It was necessary to carry out the hydrogenolysis of the tosyl derivatives under controlled and mild conditions, leaving

a part of the tosyl derivative unchanged to poison the nickel catalyst in order to avoid undesirable side reactions. The crude reaction mixture was treated with alcoholic caustic potash to hydrolyse the unchanged tosyl derivative, and the mixture of hydroxyflavones separated by chromatography. Thus, by the hydrogenolysis of the 7-tosyl ester (XVIII) of chrysin, a mixture of 5-hydroxyflavone (XX) and chrysin was obtained ; when the mixed flavones were dissolved in benzene and chromatographed on Florex xxx (an extruded fuller's earth supplied by the Floridin Co., Inc.), development and elution with benzene yielded 5-hydroxyflavone (XX) in a yield of about 25% calculated on the quantity of the tosyl derivative (XVIII) consumed in the reaction. Elution with ethyl acetate then led to the recovery of the more strongly adsorbed chrysin. The 7-tosyl ester (XIX) of galangin-3-methyl ether on Raney-nickel treatment and hydrolysis of the product yielded galangin-3-methyl ether and 5-hydroxy-3-methoxyflavone (XXI), readily separable by chromatography. Galangin-3-methyl ether and 5-hydroxy-3-methoxyflavone can also be separated by taking advantage of the sparing solubility of the former in benzene.

(XIX) (XXI)



(XXII)

Kurth and Hubbard[51] isolated from *Ponderosa* pine bark a bright yellow colouring matter, to which they assigned the structure 3 : 5 : 8 : 3′ : 4′-pentahydroxyflavone (XXII) which was synthesised by the indicated route, and found to be different in its m.p. and other properties from the *Ponderosa* colouring matter[21]. Further work has shown that the latter is a complex mixture, from which quercetin, taxifolin (2 : 3-dihydroquercetin), and two new colouring matters, 6-methylquercetin (pinoquercetin) and 6-methylmyricetin (pinomyricetin) have so far been isolated[52].

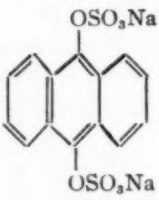
A New General Method for the Reduction of Quinones to the corresponding Hydrocarbon Derivatives

The action of Raney nickel on the sulphuric esters of phenols has been studied to determine if sulphuric esters can be used as intermediates in place of tosyl esters for the removal of phenolic hydroxyl groups[53]. *p*-Hydroxybenzoic acid

was sulphated using pyridine and chlorosulphonic acid. The sulphuric ester was not isolated, but converted into the dipotassium salt (XXIII), which was treated with Raney nickel and hydrogen. From the reaction mixture benzoic acid (65%) and a little *p*-hydroxybenzoic acid were isolated.

The hydrogenolysis of (XXIV), the disodium salt of the disulphuric ester of anthrahydroquinone, was then examined. An aqueous solution of the disulphuric ester was treated with Raney nickel and hydrogen for 4 hours at room temperature and filtered. Benzene extraction of the nickel residue after deactivation gave a mixture of 1:2:3:4-tetrahydroanthraquinone and hydrogenated anthracene; the latter was then dehydrogenated by selenium to anthracene in an overall yield of 30%. From the aqueous filtrate, after oxidation with sodium nitrite and sulphuric acid, a further quantity of 1:2:3:4-tetrahydroanthraquinone was recovered, indicating that hydrogenation of anthrahydroquinone disulphuric ester to 1:2:3:4-tetrahydroanthrahydroquinone disulphuric ester also took place as a side reaction. The formation of a quinonoid derivative, because of the incomplete hydrogenolysis of the ester even when a large amount of Raney nickel was used, was practically eliminated by carrying out the reaction using Raney alloy and aqueous alkali instead of Raney-nickel catalyst. This modification gave an excellent yield of hydrogenated anthracene (85%) which could be readily dehydrogenated to anthracene.

(XXIII)



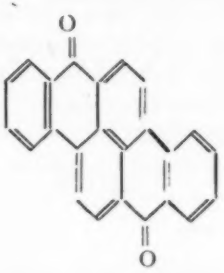
(XXIV)

A new general method for the conversion of quinones to the corresponding hydrocarbons through the disulphuric esters of the leuco derivatives thus became available[53]. The cleavage of sulphuric esters by Raney nickel affords an alternative route for the preparation of hydrocarbons, having advantages over phosphorus-hydriodic acid and zinc dust distillation methods, which use high temperatures and may cause structural rearrangement. Sulphuric esters of leuco derivatives of over thirty vat dyes are available commercially and numerous analogues can be readily prepared, providing suitable raw materials for the preparation of polycyclic hydrocarbons, azahydrocarbons, etc., which are of interest in connection with their chemical reactivity, electronic structure, absorption spectra, photochemical behaviour and carcinogenic properties.

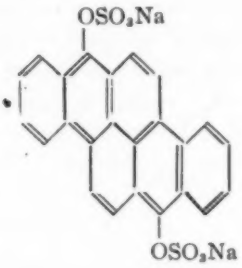
Dibenzpyrenes

Reduction of Indigosol Golden Yellow IGK (XXVI), the disodium salt of the disulphuric ester of Indanthrene Golden Yellow GK (3:4:8:9-dibenzpyrene-5:10-quinone, XXV), by means of Raney alloy and aqueous alkali afforded an excellent

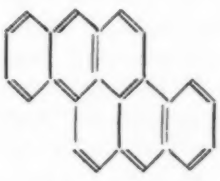
yield (80%) of a mixture of hydrogenated hydrocarbons, which were separated by chromatography into hexahydrodibenzpyrene (m.p. 240-41°) and decahydrodibenzpyrene (m. p. 235-36°). By treatment with iodine and sodium acetate in boiling nitrobenzene, the mixture of hydrogenated hydrocarbons was dehydrogenated to 3 : 4 : 8 : 9-dibenzpyrene (XXVII), prepared earlier by other workers from the quinone (XXV) by zinc dust distillation, Clar reduction, and reduction with phosphorus and hydriodic acid.



(XXV)



(XXVI)



(XXVII)

For determining the constitution of commercial anthraquinonoid vat dyes, the Raney-nickel hydrogenolysis of their leuco sulphuric esters is sometimes a useful approach. One example is Mayvat Brilliant Red AF, recently marketed in the United States as an "entirely new homogeneous anthraquinone vat colour". A preliminary examination of the dye, which crystallised from *o*-dichlorobenzene in red needles, showed that it was a halogenated quinone containing chlorine and bromine, but no nitrogen or sulphur. The leuco sulphuric ester was prepared by the usual Soledon process[54] and reduced with Raney alloy and caustic soda solution. The product was a mixture of hydroaromatic compounds, dehydrogenation of which with selenium led to 3 : 4 : 9 : 10-dibenzpyrene (XXVIII), identified by its m.p. and absorption spectrum[55]. On shaking Mayvat Brilliant Red AF with caustic soda solution and hydrogen in presence of a catalytic amount of Raney nickel, dehalogenation took place, and the product after crystallisation was identified as 3 : 4 : 9 : 10-dibenzpyrene-5 : 8-quinone (XXIX). Mayvat Brilliant Red AF therefore proved to be a chloro-bromo derivative of the quinone (XXIX), and this dye is a very convenient source for the hydrocarbon (XXVIII), which is currently of interest because of its powerful carcinogenic properties[56]. Indanthrene Scarlet 4G has been stated[57] to be the dibromo derivative of (XXIX), but a sample kindly supplied by Cassella Farbwerke, Mainkur, has been found to contain both chlorine and bromine. Dehalogenation yielded the quinone

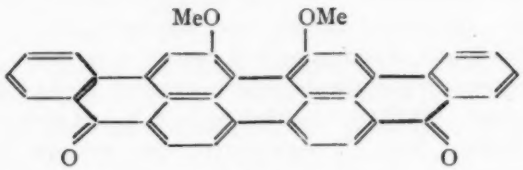
(XXIX). Indanthrene Scarlet 4G and Mayvat Brilliant Red AF dye have substantially different shades and they exhibit different colours in sulphuric acid ; the number and position of the halogen atoms, which must be responsible for these differences, are under investigation. The quinone (XXIX) can be reduced to the hydrocarbon (XXVIII) smoothly and in excellent yield by means of aluminium *cyclo*hexoxide in boiling *cyclo*hexanol, which Coffey and Boyd have shown to be effective for reducing anthraquinone to anthracene and anthanthrone to anthanthrene[58].

(XXIX)

(XXVIII)

16 : 17-Dimethoxyviolanthrene

A quinone which can be reduced to the corresponding hydrocarbon derivative by aluminium *cyclo*hexoxide in *cyclo*hexanol is the important dye 16 : 17-dimethoxyviolanthrone (Caledon Jade Green ; XXX). Alternatively, when the sodium salt of the disulphuric ester of the leuco compound, available commercially, was treated with Raney alloy, aqueous caustic soda and toluene under specified conditions, a 50 % yield of 16 : 17-dimethoxyviolanthrene (XXXI) was obtained[59]. A notable feature of this hydrogenolysis was that, unlike the other reductions of the sulphuric esters of quinones which gave the hydrogenated hydrocarbons, the direct product of the Raney-nickel reduction was the aromatic compound (XXXI) and not a partially hydrogenated derivative. The new compound (XXXI) is of very special interest since it is an "overcrowded molecule" which is optically active and can be resolved by using the new technique of Newman[60] in which the complex with optically active 2-(2 : 4 : 5 : 7-tetranitro-9-fluorenylideneaminóóxy)-propionic acid is fractionally crystallised. The stereochemistry of Caledon Jade Green (XXX) in relation to its colour has been discusssd elsewhere[61].



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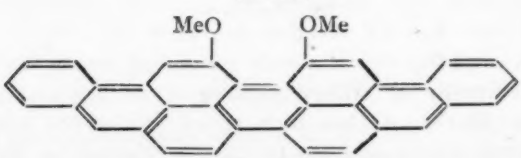
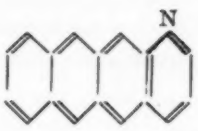


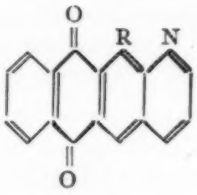
(XXXI)

Synthesis of 1-Azanaphthacene

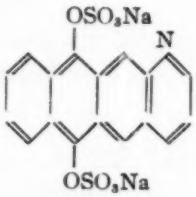
A further application of the Raney-nickel method for the reduction of quinones to the corresponding hydrocarbon derivatives is the synthesis of the hitherto unknown 1-azanaphthacene (XXXII)[62]. The Skraup reaction on 2-amino-1-chloroanthraquinone, adding arsenic pentoxide to suppress the benzanthrone reaction, gave a good yield of 12-chloro-1-azanaphthacene-6:11-dione (XXXIII). Dechlorination by means of caustic soda and sodium hydrosulphite and air oxidation of the vat yielded 1-azanaphthacene-6:11-dione (XXXIV). Treatment of the disodium salt (XXXV) of the disulphuric ester of (XXX) with Raney alloy and caustic soda at 100° gave an octahydroazanaphthacene, the absorption spectrum of which showed that it had the structure (XXXVI), and which was dehydrogenated to 1-azanaphthacene (XXXII) by prolonged heating with palladized carbon in boiling Dowtherm.



(XXXII)



(XXXIII: R = Cl)
(XXXIV: R = H)



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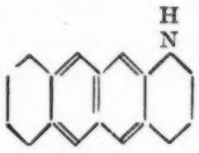
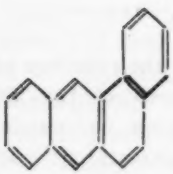


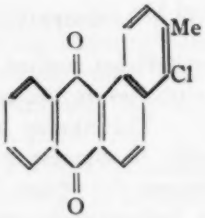
(XXXVI)

Synthesis of Benzanthracenes

The hydrogenolysis of leuco sulphuric esters of quinones by Raney alloy and aqueous alkali to the corresponding hydrocarbon derivatives has been extended to the leuco sulphuric esters of 1:2-benzanthraquinone and its derivatives for the preparation of benzanthracene and methylbenzanthracenes[59], which are of interest in connection with their carcinogenic activity and which were synthesized earlier in poor yields by much more difficult routes. Thus, the hydrogenolysis of the sulphuric ester of benzanthrahydroquinone gave a hydrogenated benzanthracene, which was dehydrogenated to 1:2-benzanthracene (XXXVII) in an overall yield of 70%.



(XXXVII)



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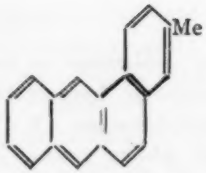
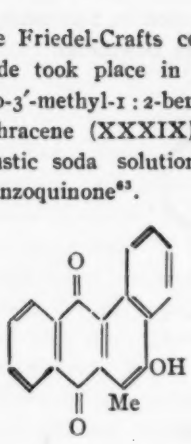
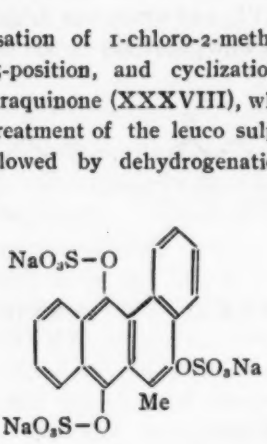


(XXXIX)

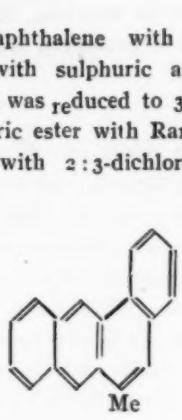
The Friedel-Crafts condensation of 1-chloro-2-methylnaphthalene with phthalic anhydride took place in the 5-position, and cyclization with sulphuric acid gave 4′-chloro-3′-methyl-1 : 2-benzanthraquinone (XXXVIII), which was reduced to 3′-methylbenzanthracene (XXXIX) by treatment of the leuco sulphuric ester with Raney alloy and caustic soda solution, followed by dehydrogenation with 2 : 3-dichloro-5 : 6-dicyanobenzoquinone[63].



(XLII)



(XLI)



(XL)

The synthesis of 4-methyl-1 : 2-benzanthracene (XL) was achieved through the trisodium salt (XLI) of the trisulphuric ester of leuco 3-hydroxy-4-methylbenzanthraquinone. The desired benzanthraquinone derivative, 3-hydroxy-4-methylbenzanthraquinone (XLII), was obtained by condensing 3-hydroxybenzanthraquinone with aqueous caustic soda, sodium hydrosulphite and formaldehyde (the Marschalk reaction)[64]. The intermediate 3-hydroxybenzanthraquinone was prepared by a slight modification of Fieser's method[65]. As a pilot experiment, the trisulphuric ester of leuco 2-hydroxyanthraquinone was reduced by Raney alloy and aqueous caustic soda to a hydrogenated anthracene, which was then dehydrogenated to anthracene, showing that nuclear hydroxyl groups in the anthraquinone series could be reduced via the sulphuric ester. The reduction of the trisulphuric ester (XLI) of leuco 3-hydroxy-4-methylbenzanthraquinone similarly gave a hydrocarbon, analysing for a hexahydro-4-methylbenzanthracene which was dehydrogenated to 4-methylbenzanthracene (XL) by boiling in benzene with dichlorodicyanobenzoquinone.

Raney-nickel reduction has proved valuable in dealing with the problem of the

constitution of morellin, the main colouring matter of the seeds of *Garcinia morella*. On the basis of a new formula, $C_{33}H_{38}O_7$, selective hydrogenation, alkaline hydrolysis, and ultraviolet and infra-red absorption data, a partial structure for morellin was suggested earlier[66]. Evidence for a 2:2-dimethylchromene ring and a 5-hydroxychromanone ring, built on a phloroglucinol nucleus, was conclusive. The chromanone ring was considered to be part of a partially hydrogenated 1:2-benzoxanthone ring system. The disposition of the ethylenic bonds and a second carbonyl group in the naphthalene moiety remains uncertain, but definite evidence for the presence of a partially hydrogenated naphthalene ring has been obtained by the use of Raney nickel. The action of Raney nickel in boiling *cyclo*hexanol on morellin gave a product (A), m.p. 172°, which was also produced by an attempted palladium-charcoal dehydrogenation of the Raney-nickel reduction product, m. p. 110-11°, described earlier. The ultraviolet absorption spectrum of (A) closely resembled the spectra of dihydrotoxicarol and hexahydro-osajin. When (A) was fused with caustic potash at 290°, two of the products were *n*-valeric acid and an acid (B), m.p. 281°, which analysed for $C_{12}H_{12}O_4$, a tetrahydronaphthalene dicarboxylic acid. Treatment of (B) with copper-bronze and quinoline with the object of effecting decarboxylation resulted in simultaneous dehydrogenation with the formation of naphthalene. The utility of copper in boiling quinoline as a reagent for dehydrogenation was demonstrated by the conversion of tetrahydronaphthalene to naphthalene. The ultraviolet absorption spectrum of the acid (B) in comparison with the spectra of benzoic acid and the three phthalic acids, and the fact that nitric acid oxidation of (B) yielded mellophanic acid (benzene-1:2:3:5-tetracarboxylic acid), showed that (B) was tetrahydronaphthalene-5:7-dicarboxylic acid.

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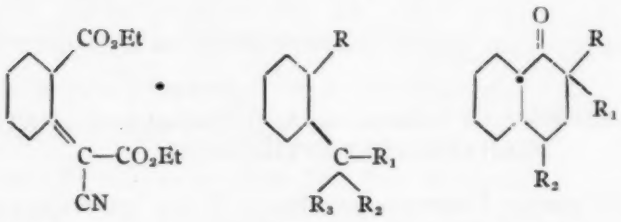
NEW SYNTHESES OF *trans-syn-cis* -AND *trans-anti-trans*-9-KETO-PERHYDROPHENANTHRENES

By Ramesh Chandra Chatterjee and Bidyut Kamal Bhattacharyya

The Mannich-Robinson reaction with 1-diethylaminobutanone-3 was applied on the β-keto-diester (III: R=H; R_1=R_2=CO_2Me), prepared from (II: R=R_1=CO_2Et; R_2=H; R_3=CN) by cyanoethylation, hydrolysis, esterification and the Dieckmann cyclisation, to yield 2-γ-ketobutyl-2 : 4-dicarbomethoxy-*trans*-1-decalone, which on cyclisation, followed by esterification, furnished (IV: R=CO_2Me). The latter compound on reduction with lithium aluminium hydride, followed by dehydrogenation, yielded the 9-methylphenanthrene. The compound (IV: R=CO_2Me) was hydrogenated to the saturated keto-esters which on Huang-Minlon's reduction yielded two different acids, the esters of which were separately subjected to the Barbier-Wieland degradation to produce (VIII) and (IX) respectively.

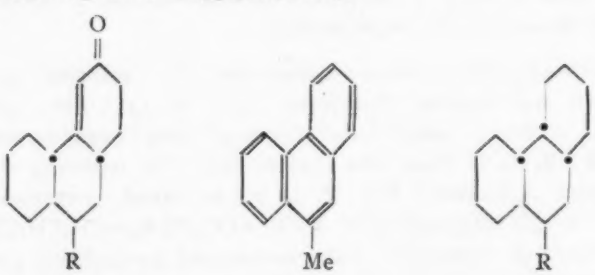
Although it has been observed that in steroid the hydrogenation of $\Delta^{9:11}$ double bond by Adams' catalyst in glacial acetic acid proceeds in a stereospecific manner to give the natural steroid configuration, *i.e.*, *trans-anti-trans* (Woodward *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 4224 ; Kendall *et al.*, *J. Biol. Chem.*, 1948, **175**, 249 ; Shoppee and Reichstein, *Helv. Chim. Acta*, 1941, **24**, 351 ; Shoppee, *ibid.*, 1940, **23**, 740), yet in the present investigation the hydrogenation of 9-carbomethoxy-1 : 2 : 3 : 4b : 5 : 6 : 7 : 8 : 8a : 9 : 10 : 10a-dodecahydrophenanthrene-3-one with palladium on charcoal was found to yield a mixture of *trans-syn-cis* and *trans-anti-trans* ring fusions of which the former was the major product.

Ethyl 2-carbethoxy*cyclo*hexylidene-1-cyanoacetate (I), prepared according to the method of Grew and Mondon (*Naturwiss.*, 1946, **11**, 333 ; *Ber.*, 1948, **81**, 279), was hydrogenated to furnish ethyl 2-carbethoxy*cyclo*hexyl-1-cyanoacetate (II : R=R_1=CO_2Et; R_2=H; R_3=CN) which was cyanoethylated by following the procedure of Bruson ("Organic Reactions", Vol. V, p. 79) to furnish γ-cyano-γ-carbethoxy-γ-(2-carbethoxy*cyclo*hexyl)-butyronitrile (II : R=R_1=CO_2Et; R_2=CH_2CH_2CN; R_3=CN). The latter compound on hydrolysis with concentrated hydrochloric acid yielded a crystalline tricarboxylic acid (II : R=R_1=CO_2H ; R_2=$CH_2CH_2CO_2H$; R_3=H). The trimethyl ester (II : R=R_1=CO_2Me ; R_2=$CH_2CH_2CO_2Me$; R_3=H) smoothly underwent the Dieckmann cyclisation with sodium dust to afford dimethyl *trans*-1-decalone-2 : 4-dicarboxylate (III : R=H ; R_1=R_2=CO_2Me) which on hydrolysis with hydrochloric acid yielded *trans*-1-decalone-4-carboxylic acid (III : R=R_1=H ; R_2=CO_2H) which was previously prepared by Novello *et al.* (*J. Amer. Chem. Soc.*, 1953, **75**, 1330) as well as by Downes *et al.* (*ibid.*, 1950, **72**, 3464) by different routes. The β-keto-diester (III : R=H ; R_1=R_2=CO_2Me) was methylated with sodium dust and methyl iodide and the methylated product (III : R=Me ; R_1=R_2=CO_2Me), thus obtained, was hydrolysed with hydrochloric acid to yield crystalline 2-methyl-*trans*-1-decalone-4-carboxylic acid (III : R=Me ; R_1=H; R_2=CO_2H).



(I) (II) (III)

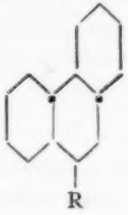
The Mannich-Robinson reaction (*J. Chem. Soc.*, 1937, 53 and subsequent papers) with 1-diethylaminebutanone-3 was applied on the dimethyl *trans*-1-decalone-2:4-dicarboxylate to give the open-chain compound, 2-γ-ketobutyl-2:4-dicarbomethoxy-*trans*-1-decalone (III: $R=CH_2CH_2COMe$; $R_1=R_2=CO_2Me$). The latter was then cyclised and decarboxylated with a mixture of concentrated hydrochloric and glacial acetic acids according to the method of Wilds and Shunk (*J. Amer. Chem. Soc.*, 1943, **65**, 469) to furnish a gummy acidic material (IV: $R=CO_2H$) which was esterified by diazomethane to yield 9-carbomethoxy-1:2:3:4b:5:6:7:8:8a:9:10:10a-dodecahydrophenanthrene-3-one (IV: $R=CO_2Me$). In order to ascertain the tricyclic skeleton of the cyclised condensation product (IV: $R=CO_2Me$), the latter was treated with lithium aluminium hydride in ethereal solution to furnish a diol, which on dehydrogenation with selenium yielded the known 9-methylphenanthrene (V) (Windaus *et al.*, *Ber.*, 1924, **57**, 1871, 1875; Haworth and Mavin, *J. Chem. Soc.*, 1932, 2720; Marvel *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 2741; Mukherji and Bhattacharyya, *J. Org. Chem.*, 1952, **17**, 1208).



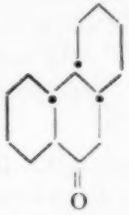
(IV) (V) (VI)

The hydrogenation of the keto-ester (IV: $R=CO_2Me$) was carried out with palladium on charcoal and the carbonyl group of the hydrogenated product was then reduced by the method of Huang-Minlon (*J. Amer. Chem. Soc.*, 1946, **68**, 2487, 1949, **71**, 3301) to yield two different acidic materials: (*a*) liquid and (*b*) solid, m.p. 192-93° in in the ratio of 9:1. In order to establish the stereochemical configurations, the two acids were separately esterified and the esters were subjected to the Grignard reaction with phenylmagnesium bromide. The carbinol obtained from the liquid acid was oxidised directly or dehydrated and then oxidised according to the method of Zeiss (*ibid.*, 1948, **70**, 858) to furnish *trans-syn-cis*-9-ketoperhy-

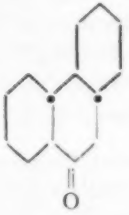
drophenantherene (VIII) (Linstead *et al.*, *J. Chem. Soc.*, 1950, 1428; *J. Amer. Chem. Soc.*, 1942, **64**, 1991 and subsequent papers; Marvel and White, *ibid.*, 1940, **62**, 2739). The carbinol from the crystalline acid was dehydrated to the unsaturated compound which was then ozonised to provide *trans-anti-trans* ketone (IX) (Bhattacharyya, this *Journal*, 1945, **22**, 85; Linstead *et al.*, *loc. cit.*).



(VII)



(VIII)



(IX)

*Experimental

Ethyl 2-Carbethoxycyclohexyl-1-cyanoacetate (II: R = R_1 = CO_2Et; R_2 = H; R_3 = CN).—To a suspension of 10% Pd—C (0.8 g.) in 95% ethanol (40 c.c.) was added a solution of ethyl 2-carbethoxy*cyclo*hexylidene-1-cyanoacetate (I, 53 g.) in an atmosphere of hydrogen. After an induction period of 35 minutes the average rate of absorption of hydrogen was 160 c.c. per hour and the total absorption was 4870 c.c. of hydrogen at 28°. The mixture was filtered and ethanol was distilled under reduced pressure. Distillation of the residual liquid afforded a colorless mobile oil, b.p. 135-40°/0.7 mm, yield 52 g. (Found: C, 62.64; H, 7.80. $C_{14}H_{21}O_4N$ requires C, 62.92; H, 7.86%).

γ-Cyano-γ-carbethoxy-γ-(2-carbethoxycyclohexyl)-butyronitrile (II: R = R_1 = CO_2Et; R_2 = CH_2CH_2CN; R_3 = CN).—A mixture of the above cyano-ester (13.4 g.), freshly distilled acrylonitrile (3.18 g.) and peroxide-free dioxane (5 g.) was cooled for 30 minutes at 0°-10°. To it was added "Triton B" (0.4 c.c.) dropwise with constant swirling. Immediately the colour of the solution turned brown. The reaction was allowed to proceed at 0°-10° for one hour and then at room temperature for 48 hours. The reaction mixture was taken up in benzene, washed thoroughly with 2*N*-HCl solution and finally with water. After removal of the solvent the liquid was distilled, b.p. 185-90°/0.7 mm; $n_D^{31.5}$ 1.4842; yield 15.0 g. (Found: C, 63.71; H, 7.62. $C_{17}H_{24}O_4N_2$ requires C, 63.75; H, 7.5%).

Methyl γ-Carbomethoxy-γ-(2-carbomethoxycyclohexyl)-butyrate (II: R = R_1 = CO_2Me; R_2 = $CH_2CH_2CO_2Me$; R_3 = H).—A mixture of the above dicayano-ester (34 g.) and HCl (conc., 300 c.c.) was heated under reflux for 50 hours. After 30 hours' refluxing the reaction mixture was homogeneous. The acidic mixture was concentrated in a steam-bath when white crystals of the tricarboxylic acid (II: R = R_1 = CO_2H; R_2 = $CH_2CH_2CO_2H$; R_3 = H), m.p. 165°, separated out. A portion of the crystalline material

* All m.p.s. are uncorrected. The U.V.-spectrum was measured by the Unicam spectrophotometer (SP 500).

was recrystallised three times from a mixture of ether and petroleum ether to afford the pure material, m.p. 171°. (Found : C, 55.65 ; H, 7.20 ; N.E., 85.0. $C_{12}H_{16}O_6$ requires C, 55.81 ; H, 6.97% ; N.E., 86). The crude acid containing ammonium chloride, obtained by evaporation, was dried and esterified by refluxing with methanolic (73 c.c.) sulphuric acid (10 c.c., *d* 1.84) for 50 hours. The cooled reaction mixture was poured into crushed ice and the precipitated oil was extracted four times with ether-benzene mixture. The solvent layer was washed successively with water, 2% ice-cold sodium hydroxide solution and finally with water. After removal of the solvent, the residual oil was distilled, b.p. 174-76°/2 mm ; $n_D^{21.5}$ 1.465 ; yield 22.7 g. (Found : C, 60.21 ; H, 8.30. $C_{15}H_{24}O_6$ requires C, 60.00 ; H, 8.0%).

Dimethyl trans-1-*Decalone*-2 : 4-*dicarboxylate* (III : R=H ; $R_1=R_2=CO_2Me$).—To a suspension of sodium dust (2.3 g.) in dry benzene (75 c.c.) was added a solution of the above triester (15 g.) in dry benzene (25 c.c.) containing dry methanol (0.5 c.c.). The mixture was then refluxed for 5 hours under nitrogen atmosphere. The sodio enolate of the β-keto-diester was insoluble in benzene. The reaction mixture was cooled and acidified with cold dilute hydrochloric acid. The benzene layer was separated and the aqueous layer was extracted thrice with ether-benzene mixture. The combined solvent was washed successively with water, ice-cold 2% sodium hydroxide solution and finally with water. The solvent was removed. Distillation of the residual liquid gave a colorless, thick, mobile oil, b.p. 155-60°/1.5 mm ; $n_D^{21.5}$ 1.4958 ; yield 9.2 g. The alcoholic solution of the liquid showed a strong violet coloration with ferric chloride solution. (Found : C, 63.01 ; H, 7.80. $C_{14}H_{20}O_5$ requires C, 62.68 ; H, 7.46%).

trans-1-*Decalone*-4-*carboxylic Acid* (III : R=R_1=H ; $R_2=CO_2H$).—A mixture of the above β-keto-diester (1.2 g.) and HCl (conc., 12 c.c.) was heated under reflux for 16 hours. The acidic mixture was diluted with water and after saturation with ammonium chloride it was repeatedly extracted with ether. The ethereal layer was then washed once with cold saturated brine solution, dried over anhydrous sodium sulphate and the solvent was removed. The liquid residue (0.8 g.) on evaporative distillation at 130-40°/0.2 mm yielded a yellow semi-solid mass which was then kept under petroleum ether and scratched with a glass rod, when a solid, m.p. 141°, was obtained. This on four crystallisations from a mixture of ether and petroleum ether afforded the pure white material, m.p. 156.5-157° [lit. m.p. 153.2-54.7°]. (Found : C, 67.51 ; H, 8.42. Calc. for $C_{11}H_{16}O_3$: C, 67.34 ; H, 8.16%).

The *semicarbazone*, prepared by the sodium acetate method, was crystallised three times from dilute methanol to furnish the pure material, m.p. 215-16° (decomp.). (Found : C, 56.52 ; H, 7.84. $C_{12}H_{19}O_3N_3$ requires C, 56.91 ; H, 7.51%).

The 2 : 4-*dinitrophenylhydrazone* was prepared directly from the semicarbazone (0.1 g.) and 2 : 4-dinitrophenylhydrazine (0.1 g.) in 95% ethanol (10 c.c.) by refluxing with 6 drops of HCl (conc.). Two recrystallisations from a mixture of alcohol and ethyl acetate furnished orange needles, m.p. 215° (decomp.) [lit. m.p. 210.5-213° (decomp.), and m.p. 200° (decomp.)].

Dimethyl 2-Methyl-trans-1-*decalone*-2 : 4-*dicarboxylate* (III : R = Me ; $R_1=R_2=CO_2Me$).—(*a*). To a cold suspension of sodium dust (0.9 g.) in dry benzene (40 c.c.) was added a solution of the β-keto-diester (8.7 g.) in dry benzene (15 c.c.) dropwise with swirling in an atmosphere of nitrogen, and the reaction was allowed to proceed for 20 hours at room temperature To the white precipitate of the sodio enolate was added methyl iodide (6 c.c.) and the reaction mixture was refluxed for 5 hours. It was cooled, diluted with water and the aqueous layer was extracted twice with benzene. After removal of the solvent, the residual oil was distilled, b.p. 160°/1.5 mm ; n_D^{23} 1.483 ; yield 6.3 g. The liquid gave no positive ferric chloride coloration in alcoholic solution. (Found : C, 63.58 ; H, 8.0. $C_{15}H_{22}O_5$ requires C, 63.86 ; H, 7.80%).

(*b*). To the sodio enolate, prepared from trimethyl ester (11.5 g.), sodium dust (1.9 g.), dry benzene (75 c.c.) and methanol (0.5 c.c.), as described before, was added methyl iodide (10 c.c.), and the mixture was refluxed for 5 hours, cooled, worked up as above and distilled ; yield 7.3 g.

2-*Methyl*-trans-1-*decalone*-4-*carboxylic Acid* (III : R=Me ; R_1=H ; $R_2=CO_2H$).—A mixture of the above methylated keto-diester (2.7 g.) and HCl (conc., 30 c.c.) was refluxed for 16 hours. On cooling, a solid acid (1.7 g.), m.p. 166°, separated out from the solution, and a further quantity (0.3 g.) of the acid was obtained by repeated extraction of the aqueous acidic layer with ether. The crude acid after four crystallisations from a mixture of ether and petroleum ether afforded the pure material, m.p. 183-84°. (Found : C, 68.38 ; H, 8.42. $C_{12}H_{18}O_3$ requires C, 68.57 ; H, 8.57%). This keto-acid did not furnish any semicarbazone by the usual methods.

2-γ-*Ketobutyl*-2 : 4-*dicarbomethoxy*-trans-1-*decalone* (III : R = CH_2CH_2COMe ; $R_1=R_2=CO_2Me$).—To cold sodium methoxide, prepared from sodium (0.46 g.) in dry benzene (20 c.c.) and absolute methanol (10 c.c.) by refluxing, was added dropwise a solution of the β-keto-diester (III : R=H ; $R_1=R_2=CO_2Me$; 5.3 g.) in dry benzene (20 c.c.) with constant swirling under nitrogen atmosphere and the reaction was allowed to proceed for 20 hours at room temperature. To the insoluble sodio enolate of the β-keto-diester, cooled in an ice-bath for 1 hour, was added slowly a solution of the methiodide, prepared from redistilled 1-diethylaminobutanone-3 (5 g.) in absolute methanol (20 c.c.), with constant swirling. All the sodio enolate dissolved after 30 minutes' swirling. The reaction mixture was then allowed to stand at room temperature for 24 hours to complete the reaction. The clear straw-yellow solution was diluted with water and extracted thrice with benzene. The solvent layer was washed with HCl (dil.) and finally with water. After removal of the solvent, the residual liquid was fractionated : (1) b.p. 150-60°/1.2 mm ; 0.85 g. and (2) b.p. 200-205°/1.2 mm ; n_D^{23} 1.4960 ; 4.35 g. The viscous sticky mass could not be crystallised. (Found : C, 64.15 ; H, 7.87. $C_{18}H_{26}O_6$ requires C, 63.90 ; H, 7.70%).

9-*Carbomethoxy*- 1 : 2 : 3 : 4b : 5 : 6 : 7 : 8 : 8a : 9 : 10 : 10a-*dodecahydrophenanthrene*-3-*one* (IV : R=CO_2Me).—A solution of the above condensation product (2 g.) in a mixture of HCl (conc., 20 c.c.) and glacial acetic acid (60 c.c.) was refluxed for 14 hours under nitrogen. Heating for a longer period decreased the yield. After removal of most of the

acetic acid and HCl under reduced pressure, the residue was diluted with ice-water and the aqueous layer was extracted several times with ether. The solvent layer was washed once with brine solution and dried over anhydrous sodium sulphate. After removal of the solvent, a semi-solid mass was obtained ; λ_{max}^{alc} 236 mμ (log ε 3.8). The crude acid was then esterified with diazomethane, prepared from nitrosomethylurea (1 g.), in ethereal solution. After the evolution of nitrogen had ceased, the excess of diazomethane was destroyed by the addition of acetic acid. The ester was worked up as described before and then evaporatively distilled at 140-45°/0.8-1.0 mm ; λ_{max}^{alc} 236 mμ (log ε 3.91) ; yield 1.0 g. (Found : C, 72.91 ; H, 8.81. $C_{16}H_{22}O_3$ requires C, 73.28 ; H, 8.39%).

The *semicarbazone* of the unsaturated keto-ester was prepared in the usual way and was crystallised from dilute methanol in pure white crystals, m.p. 215° (decomp.) ; λ_{max}^{alc} 266 mμ (log ε 4.47). This semicarbazone was very light-sensitive and turned yellow on keeping in light. (Found : C, 64.31 ; H, 7.52 ; N, 13.41. $C_{17}H_{25}O_3N_3$ requires C, 63.95 ; H, 7.83 ; N, 13.18%).

9-*Methylphenanthrene* (V).—To a solution of lithium aluminium hydride (0.6 g.) in pure dry ether (20 c.c.), prepared by refluxing on the water-bath for 1 hour, was added dropwise a solution of the keto-ester (IV : R=CO_2Me; 1.26 g.) in dry ether (15 c.c.) with constant shaking. The reaction mixture was allowed to stand at room temperature for 48 hours to complete the reaction. The excess of the hydride was decomposed by adding water dropwise and then ice-cold 10% H_2SO_4 solution (50 c.c.) was added to it. The acidic layer was extracted four times with ether. The combined ether extract was successively washed with water, saturated sodium bicarbonate solution, finally with water and then dried. After removal of the solvent, a yellow, sticky, semi-solid mass (1 g.) was obtained. An intimate mixture of the above diol (0.45 g.) and powdered selenium (2 g.) was heated at 320-40° for 24 hours. The reaction mixture was cooled and the dehydrogenated product was thoroughly extracted with hot benzene. The combined benzene extract was distilled. To the residue, thus obtained, was added 95% ethanol (20 c.c.), boiled and filtered. To the hot concentrated filtrate was added a saturated alcoholic solution of picric acid (0.3 g.). The mixture was cooled when orange, needle-shaped picrate (0.2 g.), m.p. 148°, was obtained. Two crystallisations from ethanol afforded orange needles, m.p. 151° [lit. m.p. 151-53° for the picrate]. (Found : N, 10.14. Calc. for $C_{21}H_{15}O_7N_3$: N, 9.98%).

The *picrate* (0.1 g.), m.p. 148°, was decomposed by passing the benzene solution through alumina (Merck & Co., 10 g.). The alumina column was eluted with the same solvent and the combined benzene solution was distilled. The residue was dissolved in 95% ethanol (5 c.c) and allowed to stand for 18 hours when white crystals of 9-methylphenanthrene, m.p. 87°, separated out ; yield 0.07 g. The hydrocarbon was then evaporatively distilled at 100-105°/0.15-0.2 mm and the sublimate on three crystallisations from 95% ethanol afforded the pure material, m. p. 91° [lit. m. p. 90-91°]. Mixed m. p. with an authentic sample did not show any depression.

trans-syn-cis & trans-anti-trans-9-*Carboxyperhydrophenanthrene* (VI & VII : R = CO_2H).—To a suspension of 10% Pd—C (0.5 g.) in 95%ethanol (20 c.c.) was added a solution of the unsaturated keto-ester (IV : R = CO_2Me; 4.5 g.) in 95% ethanol (15 c.c.) in an atmosphere of hydrogen. When the absorption of hydrogen was slowed down after 6 hours, fresh catalyst (0.1 g.) was added to complete the hydrogenation. On working up as before, the residue was distilled, b. p. 160-65°/0.8 mm ; n_D^{33} 1.4922 ; yield 4.1 g. (Found : C, 72.44 ; H, 9.38. $C_{16}H_{24}O_3$ requires C, 72.73 ; H, 9.09%).

To a solution of the above saturated keto-ester (1.0 g.) in diethyleneglycol (10 c. c.) was added 85% hydrazine hydrate (1.5 c.c.) solution and the mixture was refluxed at 140°. After 1 hour a concentrated solution of KOH (1 g. KOH in 1 c.c. of water and 5 c.c. of diethyleneglycol) was added to the reaction mixture which was again refluxed for 1 hour. Then the condenser was taken out the temperature was raised to 200° and kept there for 1½ hours more. The reaction mixture was cooled and poured into iced HCl (5 c.c.), when a solid with adhering gum separated out. The aqueous acidic layer was saturated with ammonium sulphate and extracted four times with ether. The combined ethereal layer was washed once with brine solution, dried and distilled. The residue, left after removal of the ether, was dissolved in a mixture of ether and petroleum ether and allowed to stand at room temperature for 20 hours, when a solid acid, m.p. 190-91°, crystallised out. Two crystallisations from a mixture of ether and petroleum ether afforded the pure acid (VII : R = CO_2H ; 50 mg.), m. p. 192-93°. (Found : C, 76.33 ; H, 10.28. $C_{15}H_{24}O_2$ requires C, 76.26 ; H, 10.17%). From the mother-liquor was obtained a liquid acid (VI : R = CO_2H ; 450 mg.) which was purified by evaporative distillation at 140-45°/0.3 mm. (Found : C, 76.36 ; H, 10.50. $C_{15}H_{24}O_2$ requires C, 76.26 ; H, 10.17%).

trans-syn-cis-9-*Carbomethoxyperhydrophenanthrene* (VI : R = CO_2Me).—To a cold ethereal solution of the saturated liquid acid (VI : R = CO_2H ; 2.7 g.) was added a cold ethereal solution of diazomethane, prepared from nitrosomethylurea (2.5 g.). The ester was worked up as described before and then evaporatively distilled at 105-10°/0.2 mm ; yield 2.5 g. (Found : C, 76.52 ; H, 10.50. $C_{16}H_{26}O_2$ requires C, 76 84 ; H, 10.40%).

trans-anti-trans-9-*Carbomethoxyperhydrophenanthrene* (VII : R = CO_2Me).—The solid acid (VI : R = CO_2H; 1.5 g.), m.p. 185°, was esterified with diazomethane, prepared from nitrosomethylurea (2 g.) in ethereal solution, adopting the same method as described before. The ester was purified by evaporative distillation at 100°/0.2 mm, yield 1.5 g. (Found : C, 76.48 ; H, 10.26. $C_{16}H_{26}O_2$ requires C, 76.84 ; H, 10.40%).

trans-syn-cis-9-*Ketoperhydrophenanthrene* (VIII).—To the Grignard complex, prepared from magnesium (1.0 g.) and bromobenzene (5 c.c.) in dry ether (30 c. c.), was added a solution of the ester (VI : R = CO_2Me ; 2 g.) in thiophene-free benzene (15 c.c.) and the reaction was allowed to proceed at room temperature for 16 hours and then refluxed for 4 hours on a water-bath. It was cooled and the Grignard complex was decomposed with an excess of 25% aqueous solution of ammonium chloride and was extracted thoroughly with an ether-benzene mixture. The solvent layer was successively washed with water, saturated sodium bicarbonate solution and finally with

water. After removal of the solvent, the crude product was refluxed for 2 hours with a 10% aqueous NaOH solution. It was cooled, diluted with water and extracted thrice with ether-benzene mixture. The solvent layer was washed with water and the residue after removal of the solvents was evaporatively distilled at 140-45°/0.2 mm, yield 1.7 g. (Found: C, 86.89; H, 9.40. $C_{27}H_{34}O$ requires C, 86.63; H, 9.09%). An intimate mixture of the carbinol (0.5 g.) and fused potassium hydrogen sulphate (1.5 g.), taken in a sublimation tube, was introduced in an air-chamber, previously heated to 180° and kept at that temperature for 20 minutes under nitrogen atmosphere. The dehydrated product was evaporatively distilled at 130-35°/0.2 mm; λ_{max}^{alc} 249 mμ (log ε 4.0); yield 0.3 g.

A solution of chromic anhydride (3 g.) in a mixture of water (3 c.c.) and glacial acetic acid (G. R. quality, 21 c.c.) was added dropwise in 20 minutes to a solution of the above carbinol (1.47 g.) in glacial acetic acid (12 c.c.) at 80° and the reaction was allowed to proceed at 75-80° for 4 hours. The clear green solution was cooled, diluted with water and the product was extracted with ether. The ether extract was successively washed with water, 5% aq. NaOH solution and finally with water. After removal of the solvent, the residue was evaporatively distilled at 95°/2 mm; yield 0.3 g. The liquid ketone was then converted into the orange-red 2:4-dinitrophenylhydrazone, m.p. 230-32°, which on purification through chromatography and recrystallisation from a mixture of benzene and ethanol furnished the pure material, m.p. 236-37°, yield 0.3 g. (lit. m.p. 236-37° and 232-33°). (Found: N, 14.80. Calc. for $C_{29}H_{26}O_4N_4$: N, 14.50%). The unsaturated diphenylene compound was also oxidised with chromic anhydride in glacial acetic acid to furnish the same ketone.

Cleavage of the 2:4-dinitrophenylhydrazone was carried out according to the procedure of Djerassi (*J. Amer. Chem. Soc.*, 1949, **71**, 1003). A mixture of the above 2:4-dinitrophenylhydrazone (0.3 g.), pure chloroform (15 c.c.), pyruvic acid (N. E. 102; 21 c.c.) and approximately 4*N* anhydrous hydrobromic acid in acetic acid (2 c.c.) was kept at 50-60° for 4 hours with constant stirring, when the liquid assumed a light yellow colour. The reaction mixture was homogeneous during the reaction period. After dilution with chloroform and extraction with sodium bicarbonate solution, the organic layer was dried and distilled. The residue, containing a few crystals of 2:4-dinitrophenylhydrazone, was dissolved in excess of dry petroleum ether (b.p. 60-80°) and chromatographed on alumina (30 g.). The chromatogram was eluted with the same solvent (200 c.c.). The solvent was distilled off and the residue dried under suction. On cooling, the liquid solidified completely, m.p. 53°. The ketone on evaporative distillation at 90-95°/2 mm furnished the pure material, m.p. 56-57°, yield 0.1 g. (lit. m.p. 56.5-57°). (Found: C, 81.47; H, 10.95. Calc. for $C_{14}H_{22}O$: C, 81.55; H, 10.70%).

trans-anti-trans-9-*Ketoperhydrophenanthrene* (IX).—To the Grignard complex, prepared from magnesium (0.75 g.) and bromobenzene (4 c.c.) in pure dry ether (30 c.c.), was added a solution of the ester (VII: R = CO_2Me; 1.5 g.) in thiophene-free benzene (15 c.c.) and the reaction was carried out as described before. The carbinol (1.5 g.) was evaporatively distilled at 140-45°/0.2 mm. It was dehydrated with fused potassium

hydrogen sulphate (3 g.) using the same procedure as described before to yield the unsaturated compound (1.1 g.), evaporatively distilling at 130°/0.2 mm ; λ_{max}^{alc} 249 mμ (log ε 3.93). The latter compound (1.1 g.) was then ozonised in cold chloroform solution (30 c.c.). The ketone, thus obtained, was converted into the 2 : 4-dinitrophenylhydrazone (0.5 g.), m.p. 198-205°, purified through chromatography over alumina, and then cleaved, adopting the same procedure as before. But, instead of a solid ketone, a liquid ketone (0.2 g.) was obtained. The ketone was, however, further purified through its oxime as follows.

A mixture of the liquid ketone (50 mg.), hydroxylamine hydrochloride (100 mg.), pyridine (0.1 c.c.) and methanol (2 c.c.) was refluxed for 2 hours. After diluting the reaction mixture the oxime, m.p. 205-207°, on four crystallisations from a large amount of ethanol furnished silky needles, m.p. 226° [lit. m.p. 226-27°, 227-28°, 230-33°]. (Found : N, 6.46. Calc. for $C_{14}H_{23}ON$: N, 6.33%).

The above oxime (0.1 g.) was refluxed with 5% H_2SO_4 (10 c.c.) for 6 hours. The acidic solution was extracted with ether. The ethereal layer was washed with water, sodium bicarbonate solution and water, dried and distilled. The residue on evaporative distillation at 90°/2 mm furnished a solid ketone, m.p. 46° with an adhering oil. Two crystallisations from light petroleum ether yielded white needles, m.p. 49° [lit. m.p. 46-47°, 48°, 49°]. The mixed m.p. with an authentic sample of *trans-anti-trans*-9-ketoperhydrophenanthrene did not show any depression.

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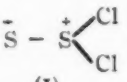
FORMATION OF SOLVATES IN SULPHUR MONOCHLORIDE

By Ram Chand, G. S. Hamdard and Kundan Lal

Formation of solvates from several anhydrous compounds in sulphur monochloride has been investigated.

Spong (*J. Chem. Soc.*, 1934, 485) put forward the view that sulphur monochloride was probably a mixture of two isomeric forms, having the structures (I) and (II).



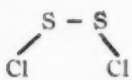
(I)

and

(II)

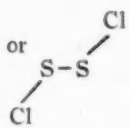
This has been supported by Giacomello (*Atti R. Accad. Lincei*, 1935, **21**, 36), Lengfeld (*Ber.*, 1895, **28**, 449), Meuwsen (*Ber.*, 1935, **68**, 121) and Stamm (*Ber.*, 1935, **68**, 673).

Electron diffraction studies (Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360) have shown that in the vapour phase sulphur monochloride has structures (III) or (IV).

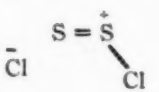


(III)

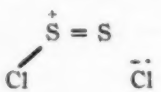
or



(IV)



(V)



(VI)

Syrkin and Dyatkina ("Structure of Molecules", Butterworth Scientific Publications, 1950) on the basis of calculations of bond energies have shown that there is a possibility of the existence of ionic structures (V) and (VI) in addition to the homopolar structures (III) and (IV).

If these ionic structures exist in sulphur monochloride, it is natural to expect that it will show some of the properties common to polar solvents. In the present work formation of solvates in sulphur monochloride has been studied.

Sulphur monochloride on coming in contact with anhydrous aluminium chloride reacts exothermally, forming a compound $AlCl_3.2S_2Cl_2$, which is only slightly soluble in it and separates out as a thick red liquid, heavier than sulphur monochloride. This solvate was prepared by Ruff and Golla (*Z. anorg. allgem. Chem.*, 1924, **138**, 17). On heating it strongly they obtained $AlCl_3.S_2Cl_2$. It has, however, been

observed that on controlled heating at 135-40°, the disolvate $AlCl_3.2S_2Cl_2$ loses a molecule of sulphur monochloride and changes to a monosolvate, $AlCl_3.S_2Cl_2$, according to

$$AlCl_3.2S_2Cl_2 \rightarrow AlCl_3.S_2Cl_2 + S_2Cl_2.$$

It is a red crystalline solid and with more sulphur monochloride changes back to disolvate.

Anhydrous ferric chloride has also been found to form a disolvate, $FeCl_3.2S_2Cl_2$, a dark pungent solid which is quite stable up to 200°. In earlier attempts to prepare a compound of sulphur monochloride with ferric chloride, Ezdakov (*Chem. Abs.*, 1942, **36**, 5439[2]) bubbled chlorine through the reaction mixture. The compound, thus obtained, $FeCl_3.2SCl_4$, is in fact a compound derived from the unstable SCl_4 rather than from sulphur monochloride. In Table I is shown a list of solvates prepared from different anhydrous compounds.

Arsenic trichloride and stannic chloride have been found to be freely miscible with sulphur monochloride, while phosphoryl chloride, which is also freely miscible with sulphur monochloride, forms a compound containing sulphur (composition not definite).

Apart from these inorganic compounds, some organic bases as pyridine and α-picoline also have been found to afford the solvates, $C_5H_5N.S_2Cl_2$ and $C_6H_7N.2S_2Cl_2$. These solvates have a low solubility in sulphur monochloride and crystallise out on cooling.

EXPERIMENTAL

Sulphur monochloride used in the present work was redistilled over elementary sulphur to remove any sulphur dichloride which might be present there. Other chemicals used for the preparation of solvates were dehydrated according to the methods (*a* to *e*) given in the literature :

(*a*) $AlCl_3$ and $FeCl_3$ were sublimed in a slow current of Cl_2.

(*b*) $CuSO_4$ CuO and BiOCl heated to constant weights.

(*c*) $CuCl_2$ heated in a current of Cl_2 gas

(*d*) $CoCl_2$, $ZnCl_2$, $MnCl_2$, $CaCl_2$, $BaCl_2$, $CdCl_2$ and $SrCl_2$ were dehydrated by heating in a current of dry HCl gas.

(*e*) Pyridine and α-picoline distilled over solid KOH.

To prepare the solvates, the solute (about 5 g.) was slowly added to sulphur monochloride (100 c.c.) in a 250 c.c. standard-joint pyrex flask fitted with a reflux condenser and a $CaCl_2$-tube to avoid all contact with moist air. The flask, if required, was cooled during the process of addition. The mixture was refluxed for 2 hours and then cooled. The solid separating out was filtered in dry atmosphere and kept in vacuo to remove the excess of adhering sulphur monochloride.

All these manipulations and transfers were done in a dry box. The compounds were analysed according to the standard methods and the results are shown in Table I.

TABLE I

Substance taken.	Solvate formed.	Calc.	Found.	State of the substance formed.
$AlCl_3$ (5 g.)	$AlCl_3.2S_2Cl_2$ (14 g.)	Al: 6.60% Cl: 61.00	6.70% 60.23	Red liquid.
	$AlCl_3.S_2Cl_2$ (9 g.) (m.p. 168°)	Al: 10.10 Cl: 66.00	10.00 65.50	Red crystalline solid.
$FeCl_3$ (5 g.)	$FeCl_3.2S_2Cl_2$ (11 g.)	Fe: 12.95 Cl: 57.40	12.80 56.76	Dark solid.
$CuCl_2$ (5 g.)	$CuCl_2.S_2Cl_2$ (5 g.)	Cu: 23.56 Cl: 52.69	23.66 52.22	Brick-red solid.
$CoCl_2$ (5 g.)	$CoCl_2.2S_2Cl_2$ (12 g.)	Co: 14.70 Cl: 53.20	14.70 52.40	Pink solid.
$ZnCl_2$ (5 g.)	$ZnCl_2.S_2Cl_2$ (8.5 g.)	Zn: 23.50 Cl: 52.40	24.00 51.60	Yellowish white solid.
$MnCl_2$ (5 g.)	$MnCl_2.S_2Cl_2$ (9 g.)	Mn: 21.00 Cl: 54.40	20.90 54.10	Buff-coloured solid.
$CaCl_2$ (4 g.)	$CaCl_2.8S_2Cl_2$ (24 g.)	Ca: 3.36 Cl: 53.65	3.39 54.10	White crystalline solid.
$BaCl_2$ (5 g.)	$BaCl_2.4S_2Cl_2$ (19 g.)	Ba: 18.30 Cl: 47.40	18.60 46.80	Light buff-coloured solid.
$CdCl_2$ (5 g.)	$CdCl_2.2S_2Cl_2$ (9.5 g.)	Cd: 24.70 Cl: 47.90	24.50 47.10	Greyish white solid.
$SrCl_2$ (6 g.)	$SrCl_2.S_2Cl_2$ (8 g.)	Sr: 29.80 Cl: 48.30	29.50 47.90	Yellowish white solid.
$CuSO_4$ (5 g.)	$2CuSO_4.S_2Cl_2$ (7 g.) ($CuSO_4.\frac{1}{2}S_2Cl_2$)	Cu: 27.90 Cl: 15.60	28.00 15.40	White crystalline solid.
CuO (5 g.)	$CuO.S_2Cl_2$ (12 g.)	Cu: 29.60 Cl: 33.10	30.10 33.26	Dark solid.
BiOCl (5 g.)	$BiOCl.S_2Cl_2$ (6.5 g.)	Bi: 52.80 Cl: 26.99	52.20 26.50	Yellowish white solid.
Pyridine (5 g.)	$C_5H_5N.S_2Cl_2$ (12 g.)	S: 29.90 Cl: 33.17	30.00 33.72	Reddish yellow crystalline solid.
α-Picoline (4 g.)	$C_6H_7N.2S_2Cl_2$ (13 g.)	S: 35.26 Cl: 39.19	34.99 39.23	Dark liquid.

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ULTRAVIOLET ABSORPTION SPECTRA OF SULPHONES. PART II. EFFECT OF CONJUGATION

By V. Baliah and Sp. Shanmuganathan

The ultraviolet absorption spectra of many $\alpha:\beta$- and $\beta:\gamma$ unsaturated sulphones have been recorded and analysed. There is significant conjugative interaction between the sulphonyl group and ethylenic link in the excited state of $\alpha:\beta$-unsaturated sulphones. In $\beta:\gamma$-unsaturated sulphones, in spite of the methylene group insulating the two chromophores, the π-electrons of the ethylenic link appear to be considerably perturbed by the inductive effect of the sulphonyl group. The absorption spectra of the sulphones, $X.C_6H_4.CH = CH.SO_2.C_6H_4.CH_3$-*p*, where X = *p*-$OCH_3$, *p*-Cl, *p*-$NO_2$ and *m*-NO_2, have been determined with a view to ascertaining the structural effects. The data are interpreted on the basis of the polar effects of the substituents and the sulphonyl group. The changes that occur in the absorption spectra of methylphenyl sulphone on introduction of substituents in the *ortho*, *meta* and *para* positions of the phenyl group have been studied.

In the present investigation the absorption spectra of a number of $\alpha:\beta$- and $\beta:\gamma$-unsaturated sulphones in ethanol solution have been recorded. The object in choosing these sulphones is to find out (1) the effect on absorption of extended conjugation involving the sulphonyl group, and (2) the effect on absorption of the introduction of a methylene group between $-SO_2-$ and the other conjugating group. The effect of increased conjugation on K-bands in sulphones may be seen from the absorption spectra recorded in Table I.

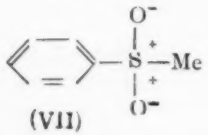
TABLE I

	Sulphones.		$\lambda_{max.}$	$\epsilon_{max.}$
(I).	$Ph.SO_2.Me$	...	* 217 mμ	6,700
(II).	$Ph.CH=CH.SO_2.Me$	...	264	20,700
(III).	$Ph.CH=CH.CH=CH.SO_2.Me$	...	300	40,200
			229	13,400
(IV).	$Ph.SO_2.C_6H_4.Me$-*p*	...	* 241	17,700
(V).	$Ph.CH=CH.SO_2.C_6H_4.Me$-*p*	...	280	26,500
			216	18,400
(VI).	$Ph.CH=CH.CH=CH.SO_2.C_6H_4.Me$-*p*	...	307	33,300
			232	16,800

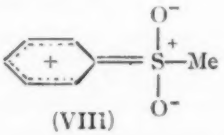
* K-band only is given.

It may be of interest to compare the absorption spectra of (I), (II) and (III) with those of benzene, styrene and 1-phenylbutadiene (Braude, *Ann. Rep. Chem. Soc.*, 1945, **42**, 105). The additional conjugation arising from attachment with $Me.SO_2-$ group is seen to cause a bathochromic shift of about 20 mμ in each case. The shift is 40 to 45 mμ when a -CHO or a $CH_3.CO-$ group is attached to phenyl (Braude and Forbes, *J. Chem. Soc.*, 1955, 3776; Braude, *loc. cit.*) or styryl group (Gillam and Stern, "Electronic Absorption Spectroscopy", Arnold, London, 1954, p. 126; Lowrey, Moureu and MacConkey, *J. Chem. Soc.*, 1928, 3167). The bathochromic shift is about 50 mμ when $-NO_2$ conjugates with phenyl, and about 30 mμ for -CN and -COOH groups (Braude, *loc. cit.*). Thus, it is seen that the conjugating ability of the $-SO_2-$ group is least among these electron-withdrawing groups. A possible explanation for this

is that in the excited state, the stabilisation for sulphones, arising out of resonance, may not be as high as in the case of nitro compounds, aldehydes, ketones, etc. Structures (VII) and (VIII) make singnificant contributions to the ground state and excited state respectively.



(VII)



(VIII)

The formation of a π-bond between sulphur and oxygen in (VIII) involves $3d$ and $2p$ orbitals. According to the principle of overlapping, a $3d$-$2p$ π-bond is less readily formed than a $2p$-$2p$ π-bond. Hence, electronic excitation of sulphones does not occur with the same facility as that of aldehydes or ketones or nitro compounds.

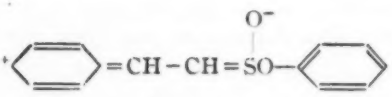
The effect caused by the introduction of a $-CH_2-$ group between $-SO_2-$ and ethenyl groups (*i.e.*, the effect of insulation) may be seen from the absorption spectra of the pairs of $\alpha:\beta$- and $\beta:\gamma$-unsaturated sulphones (Nos. 1-8) listed in Table II.

TABLE II

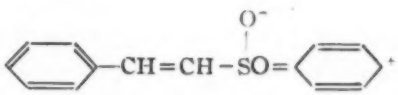
Sulphones.	$\lambda_{max.}$	$\epsilon_{max.}$
1. Ph.CH=CH.SO_2.Me ...	264 mμ	20,700
2. Ph.CH=CH.CH_2.SO_2.Me ...	294	1,400
	256	23,400
	217	14,200
3. Ph.CH=CH.SO_2.Ph ...	275	26,000
	218	16,300
	215	17,100
4. Ph.CH=CH.CH_2.SO_2.Ph ...	294	1,900
	258	23,000
	212	24,500
5. Ph.CH=CH.SO_2.C_6H_4Me-*p* ...	280	26,500
	216	18,400
6. Ph.CH=CH.CH_2.SO_2.C_6H_4Me-*p* ...	294	1,700
	258	22,700
	226	15,700
	218	19,900
	212	22,200
7. CH_2=CH.SO_2.Ph ...	274	1,000
	267	1,100
	261	900
	227	13,100
	225	13,200
8. CH_2=CH.CH_2.SO_2.Ph ...	265	1,200
	218	9,900
9. Ph.CH=CH.SO_2.C_6H_4Me-*p* ...	280	26,500
	216	18,400
10. *p*-$MeOC_6H_4$ CH=CH.SO_2.C_6H_4Me-*p* ...	308	30,000
	230	20,300
11. *p*-ClC_6H_4.CH=CH.SO_2.C_6H_4Me-*p* ...	285	30,300
	220	17,400
12. *p*-$NO_2C_6H_4$.CH=CH.SO_2.C_6H_4Me-*p*	298	23,900
	224	15,900
	221	15,700
13. *m*-$NO_2C_6H_4$.CH=CH.SO_2.C_6H_4Me-*p*	264	37,800
	229	18,700

In compounds 1, 3, 5 and 7, two chromophores are in conjugation. For example, in 3, styryl group is conjugated with phenylsulphonyl group. This conjugation has given rise to a new type of absorption — the absorption is not a summation of the individual chromophores. This is indeed the most important spectral characteristic of conjugation. In 2, 4, 6 and 8, where a methylene group separates the chromophores, the individual chromophores might be expected to retain their spectral characteristics. This is not wholly the case. Thus, cinnamylphenyl sulphone (4) has maximum absorption at 294, 258 and 212 mμ, whilst styrene absorbs at 282, 244 and 211 mμ and methylphenyl sulphone absorbs at 217 mμ (Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 231). There is thus a bathochromic shift of 12, 14 and 1mμ in the 282, 244 and 211 mμ bands, respectively, of styrene. Hyperchromic effects are also observed for all the bands. These spectral changes, occurring in spite of the insulation caused by a $-CH_2-$ group, must be attributed to the inductive effect of the sulphonyl group.

The spectra of the aryl-styryl or aryl-phenylbutadienyl sulphones can be better interpreted and correlated if the principal absorption band is assumed to originate from electronic oscillations from structures of the type (IX) and (X).



(IX)

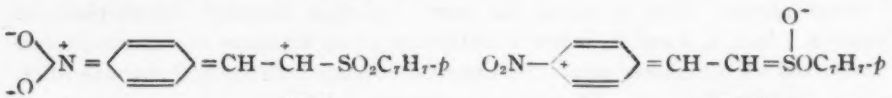


(X)

Such a formulation seems to be necessary after examining the spectra of methylstyryl sulphone, phenylstyryl sulphone and styryl-*p*-tolyl sulphone. The bathochromic shift observed in phenylstyryl sulphone, as compared with the spectrum of methylstyryl sulphone, will have to be attributed to increased resonance by the contribution of structure (X), which does not exist for methylstyryl sulphone. A further bathochromic shift, as observed, for styryl-*p*-tolyl sulphone must be expected because the electron-releasing *para*-methyl group increases the stabilisation of the excited state through an increased contribution of a structure like (X).

The effect of substituents in the aromatic nucleus attached to the ethenyl group of phenylstyryl sulphone has been studied from the spectra of compounds Nos. 9-13 listed in Table II. The *p*-methoxy- and *p*-chlorostyryl sulphones (Nos. 10 and 11) exhibit bathochromic displacements, and slight hyperchromic effects. These spectral changes are understandable in view of the fact that CH_3O- and Cl- are electron-releasing in mesomeric structures. The spectrum of *p*-nitrostyryl-*p*-tolyl sulphone (No. 12) needs a more careful analysis. At first sight it may appear that there is a considerable bathochromic displacement with a hypochromic effect (in comparison with the spectrum of styryl-*p*-tolyl sulphone). Since $-NO_2$ is an electron-attracting group, the bathochromic shift cannot be explained if the electromeric effect operates in the same direction in both Nos. 9 and 12. Actually, the electron-withdrawal by $-NO_2$ and $-SO_2-$ groups occurs in opposite directions. The $-NO_2$ group, being a more powerful electron-attractor, has a dominating influence. The

result is that *p*-nitrostyryl-*p*-tolyl sulphone will have contribution to its excited state mostly from structure (XI) and not from (XII). Thus, the spectrum is more like what is expected of *p*-nitrostyrene.



(XI) (XII)

In contrast with the *p*-nitrostyryl sulphone, *m*-nitrostyryl-*p*-tolyl sulphone has spectral resemblance to styryl-*p*-tolyl sulphone. This is due to the inability of $-NO_2$ to conjugate with vinyl group in the *m*-nitro compound. The spectral behaviour of Nos. 10 and 11 confirms also the view that the $-SO_2-$ group can conjugate with various electron-releasing groups. Further evidence in this direction is also gathered by recording the spectra of *o*-, *m*- and *p*-methoxyphenylmethyl sulphones as well as *o*-, *m*- and *p*-aminophenylmethyl sulphones (cf. Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1950, **72**, 1292; Backer and Kloosterziel, *Rec. trav. chim.*, 1953, **72**, 185, 655). The data for these compounds are summarised in Table III. The low-intensity bands observed around 280 mμ in the case of *o*- and *m*-methoxyphenyl sulphones, and around 310 mμ in the case of *o*- and *m*-aminophenyl sulphones are modified B-bands. The K-bands of the *para* isomers appear at longer wave-lengths and they are of much higher intensity too than those of the *ortho* and *meta* isomers. This is the kind of spectral relationship one would expect for the *ortho*, *meta* and *para* isomers (see Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414) if the two substituents in the benzene nucleus have opposite electromeric effects.

TABLE III

Sulphones.		$\lambda_{max.}$	$\epsilon_{max.}$
o-MeO.C_6H_4.SO_2.Me	...	283 mμ	4,200
	...	224	8,000
m-MeO.C_6H_4.SO_2.Me		287	2,900
		285	3,000
		283	3,000
	...	224	8,000
p-MeO.C_6H_4.SO_2.Me	...	240	16,500
o-NH_2.C_6H_4.SO_2.Me*		312	4,000
	...	245	8,400
m-NH_2.C_6H_4.SO_2.Me		313	2,500
		309	2,500
		249	7,900
p-NH_2.C_6H_4.SO_2.Me	...	268	19,300

* Our data agree with those of Fehnel and Carmack (*loc. cit.*).

EXPERIMENTAL

Phenylstyryl, styryl-*p*-tolyl, *p*-methoxystyryl-*p*-tolyl, *p*-chlorostyryl-*p*-tolyl and *m*-nitrostyryl-*p*-tolyl sulphones were prepared by the method of Balasubramanian

and Baliah (*J. Chem. Soc.*, 1954, 1844). Methylstyryl sulphone was prepared by the method of Balasubramanian *et al.* (*ibid.*, 1955, 3296). Phenylvinyl sulphone was prepared by the method of Smith and Davis (*J. Org. Chem.*, 1950, **15**, 824). Allylphenyl sulphone was prepared according to Otto (*Annalen*, 1894, **283**, 184). Methyl *o*-, *m*- and *p*-methoxyphenyl sulphones were prepared according to Heppenstall and Smiles (*J. Chem. Soc.*, 1938, 903). *o*-Aminophenylmethyl sulphone was obtained by the reduction of *o*-nitrophenylmethyl sulphone with $FeSO_4$ and ammonia; recrystallisation from water furnished colorless plates, m.p. 86-87° (cf. Schimmelschmidt and Thomae, U.S.P. 1,939,416/1933; *Chem. Abs.*, 1934, **28**, 1716). *m*-Aminophenylmethyl sulphone was prepared by the method of Heppenstall and Smiles (*loc. cit.*) and *p*-aminophenylmethyl sulphone, according to Goldberg and Besly (*J. Chem. Soc.*, 1945, 569). 1-Methylsulphonyl-4-phenylbuta-1 : 3-diene, m.p. 89-90.5°, was prepared as described by Shanmuganathan (Ph.D. thesis, Annamalai University, 1956, p. 62).

p-Nitrostyryl-p-tolyl Sulphone.—A mixture of *p*-tolylsulphonylacetic acid (4.3 g.), *p*-nitrobenzaldehyde (3 g.) and benzylamine (2.2 g.) in glacial acetic acid (4 c.c.) was gently heated under reflux for 30 minutes. After cooling, the product was treated with 200 c.c. of ether and left overnight. The ether layer was then separated, washed with water and dried over anhydrous $MgSO_4$. On saturating the ether solution with dry HCl, a heavy yellow oil was obtained which solidified after a few hours. The solid was filtered off, washed with ether and the filtrate allowed to evaporate. The residue (3.3 g., 55% yield) was dissolved in boiling ethanol, treated with decolorising carbon, filtered, and diluted with water. Crystallisation of the precipitated solid from methanol furnished lemon-yellow needles, m.p. 182-83°. (Found : C, 59.3 ; H, 4.5. $C_{15}H_{13}O_4NS$ requires C, 59.4 ; H, 4.3%).

Cinnamyl-p-tolyl Sulphone.—A mixture of cinnamyl chloride (18.3 g.) and sodium *p*-toluenesulphinate dihydrate (21.4 g.) in absolute ethanol (40 c.c.) was heated under reflux for 6 hours. Sodium chloride separated after 1 hour. The reaction mixture was poured into crushed ice (200 g.) and the mixture stirred vigorously. A heavy oil gradually separated. It was isolated and treated with 25 c.c. of methanol when fine needles of cinnamyl-*p*-tolyl sulphone separated. The crystals were collected and washed with a small quantity of methanol. The yield was 8.2 g. (30%). Recrystallisation from methanol afforded colorless needles, m.p. 126-26.5°. (Found : C 70.4 ; H, 5.6 ; S, 11.3. $C_{16}H_{16}O_2S$ requires C, 70.6 ; H, 5.9 ; S, 11.8%).

Cinnamylphenyl sulphone was prepared by the same method as above, using sodium benzenesulphinate dihydrate, in 33% yield. After recrystallisation from ethanol, the compound melted at 114-15°. (Found : C, 69.5 ; H, 5.3. $C_{15}H_{14}O_2S$ requires C, 69.8 ; H, 5.4%).

Cinnamylmethyl Sulphide.—A solution of sodium methyl sulphide (17.5 g.) (Windaus and Schildneck, "Organic Syntheses", Coll. Vol. II, John Wiley and Sons, New York, 1943, p. 345) in absolute methanol (100 c.c.) was heated to a

gentle reflux. The source of heat was removed and cinnamyl chloride (38.1 g.) was added dropwise with stirring at such a rate that a gentle refluxing was maintained. The mixture was heated under reflux and under stirring for 3 hours. The precipitated NaCl was filtered off and washed with methanol. The solution was concentrated on a water-bath under reduced pressure removing as much of methanol as possible. The residue was distilled under reduced pressure using an efficient fractionating column. About 18 g. of unchanged cinnamyl chloride was collected at 124-26°/14 mm. The fraction boiling at 142-44°/14 mm consisted of cinnamylmethyl sulphide. The yield was 14 g. (64%). (Found: C, 73.0; H, 7.2. $C_{10}H_{12}S$ requires C, 73.2; H, 7.3%).

Cinnamylmethyl Sulphone.—The foregoing sulphide (14 g.) was dissolved in glacial acetic acid (25 c.c.) and 30% hydrogen peroxide (50 c.c.) was added slowly under cooling over a period of 1 hour. The reaction mixture was allowed to stand overnight at room temperature. It was then heated on a water-bath at 85° for 1 hour and poured into crushed ice. The precipitated solid was collected and washed well with water. The product (5.2 g.), after recrystallisation from ethanol, furnished colorless plates, m.p. 125-25.5°. (Found: C, 60.8; H, 6.4; S, 16.0. $C_{10}H_{12}O_2S$ requires C, 61.2; H, 6.2; S, 16.3%).

1-*Phenyl*-4-p-*tolylsulphonylbuta*-1 : 3-*diene.*—A mixture of *p*-tolylsulphonylacetic acid (10.8 g.), freshly distilled cinnamaldehyde (6.6 g.), acetic anhydride (7.5 g.) and litharge (5.5 g.) was heated under reflux for 5 hours. After allowing the resulting reddish viscous liquid to remain for 2 days at room temperature, methanol (250 c.c.) was added and the mixture vigorously stirred. The pale yellow precipitate was allowed to remain overnight, collected at the pump, washed first with methanol (30 c.c.) and then with water. The product weighed 2.1 g. (15%). Recrystallisation from methanol gave colorless needles, m.p. 138-38.5°. Chodroff and Whitmore (*J. Amer. Chem. Soc.*, 1950, **72**, 1075) who prepared this compound by a different method, report m.p. 134.5-35.5°. (Found: C, 71.8; H, 5.6; S, 10.9. Calc. for $C_{17}H_{16}O_2S$: C, 71.8; H, 5.7; S, 11.3%).

Ultraviolet Absorption Measurements.—The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, model DU. All the measurements were made in 95% ethanol solution. The alcohol was purified by distillation after treatment with lead acetate and sodium hydroxide.

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PHENOLIC OXIDATION. PART II. METAL HYDRIDE REDUCTION OF DEHYDRO-*bis*(2-HYDROXY-1-NAPHTHYL)-METHANE

By J. N. Chatterjea

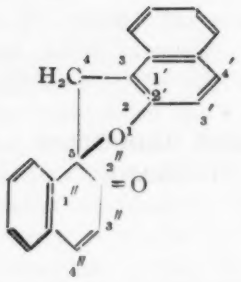
Dehydro-*bis*(2-hydroxy-1-naphthyl)-methane has been reduced with metal hydrides and the transformation of the products interpreted in terms of Pummerer's structure for the dehydro compound.

Oxidation of phenols has received considerable attention of chemists. In particular, it has been the subject of great significance in biogenetic processes (Erdtman, *Annalen*, 1933, **503**, 283 ; Harington, *J. Chem. Soc.*, 1944, 193 ; Robinson, "The Structural Relations of Natural Products", Oxford University Press, 1955, et seq). Only recently, a new interpretation of the constitution of an oxidative dimer of *p*-cresol led to a simple two-step synthesis of usnic acid by Barton and his co-workers (*J. Chem. Soc.*, 1956, 530). In an earlier paper* (this *Journal*, 1950, **27**, 375) dehydro-*bis*(2-hydroxy-1-naphthyl)-methane, an oxidation product of the phenol (III), was subjected to catalytic hydrogenation and the results assessed in terms of Pummerer's expression (I) for the compound (*Ber.*, 1914, **47**, 3477). In the present communication the action of specific carbonyl-reducing agents has been studied with a view to examining the stability of the dihydrofuran ring.

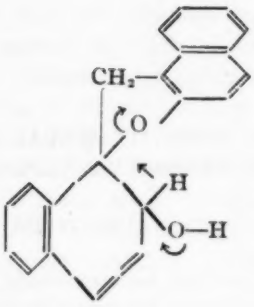
Both the Meerwein and lithium aluminium hydride reduction afforded only one unsaturated alcohol (II), m.p. 168-69° (designated A ; the product by Meerwein's method was always purer) *without* affecting the oxide linkage in contrast to catalytic methods. By using sodium or potassium borohydride in methanol, another isomeric unsaturated alcohol, m.p. 144° (designated B) was obtained in addition, and separated with some difficulty. These isomers are found to be chemical individuals and not polymorphs. The U.V. absorption spectra of both these compounds were very similar, both exhibiting a *maxima* at 235 mμ ; the I.R. spectrum (Experimental) showed some divergence. The 3″-bromo derivative of (I) on reduction with potassium borohydride also afforded a stereoisomeric mixture from which one isomer was obtained pure. In this case also the oxide link remained intact.

The above mentioned isomers, A and B, were smoothly oxidised by manganese dioxide in chloroform to (I). The Oppenauer oxidation with benzoquinone as the hydrogen acceptor was tried on (A), and a mixture of (A) and (B) ; in both cases a quantitative yield of (I) resulted. Oxidation with either acetone or *cyclo*hexanone was not possible; the products formed in these experiments were *bis*(2-hydroxy-1-naphthyl)-methane (III), formed by pinacolic electron displacement (as shown), and 1 : 2-7 : 8-dibenzoxanthene (IV), obviously formed from (III). The formation of these compounds was traced as due to the action of acid on (II), the driving force being the aromatisation of the reduced ring.

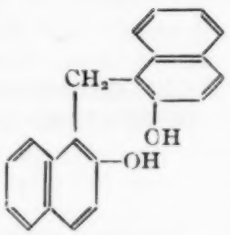
* This paper may be regarded as Part I of this series.



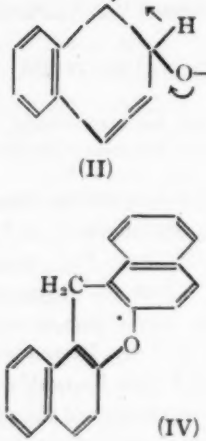
(I)



(II)



(III)



(IV)

In the light of these results, the two isomeric compounds, (A) and (B), are considered to be diastereoisomeric alcohols, the formation of which incidentally confirms the asymmetric nature of (I) on account of the presence of a spiran carbon atom (Aschan, *Ber.*, 1902, **35**, 3389 ; Leuchs, *Ber.*, 1922, **55**, 2131 ; Sutter and Wizkmann, *Annalen*, 1935, **519**, 97). The formation of two isomers by borohydride reduction against one by lithium aluminium hydride or the Meerwein reduction cannot be reconciled with the recent generalisations of Dauben *et al.* (*J. Amer. Chem. Soc.*, 1956, **78**, 2579) regarding the stereochemistry of hydride reduction. Should steric factors on account of the spiran ring play an effective part, the formation of the initial complex should depend on "steric approach control", and accordingly, the greater effective size of borohydride species should have favoured the formation of one isomer more than the other.

On reduction with lithium aluminium hydride—aluminium chloride mixture (cf. Brown, *Chem. & Ind.*, 1956, 1307), (I) gave mainly the phenol (III) by cleavage of the oxide link together with a small quantity of (A). None of the expected reduction product (=CO $\dashrightarrow$ = CH_2) appears to have been formed.

On catalytic hydrogenation, both (A) and (B) absorbed one mole of hydrogen, giving rise to corresponding isomeric saturated alcohols, one of which (from B) was identical with that obtained by direct catalytic reduction from (I) ; the other (from A) slowly passed in alcoholic solution or better *via* the benzoyl derivative, into the stable isomer. The *cyclo*hexene ring of this compound can assume puckered configuration, and it is likely that the hydroxyl group of the stable epimeride occupies the more thermodynamically stable equatorial conformation.

*EXPERIMENTAL

Metal Hydride Reactions

(*i*). *With Lithium Aluminium Hydride*: *Formation of 2″-Hydroxy-1″ : 2″-dihydronaphthalene(1″: 5)-spiro 4 : 5-dihydronaphtho-(1′: 2′-2 : 3)-furan* (II).—Lithium aluminium hydride (50 mg.) was added to a stirred suspension (0.2 g.) of the dehydro compound (I) in ether (15 c.c.). All the material gradually passed into a colorless solution which was then decomposed with ice-cold 10% HCl; the ethereal layer was washed with alkali (no phenolic material) and the residue after removal of ether furnished the *alcohol* (II) which crystallised from ethanol in small prisms, m.p. 166-67°, identical with the Meerwein reduction product, mentioned below. The compound dissolved in sulphuric acid with an orange-yellow colour, exhibiting an intense green fluorescence. (Found: C, 83.7; H, 5.3. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.5%). *I. R. spectrum*: Bands at 2.89S, 5.93M, 6.13S, 6.92S, 7.32M, 8.04M, 9.25M, 10.14S, 10.47S, 11.28M, 21.96 M, 12.31M and 12.65 Mμ.

The Meerwein reduction was done by boiling a mixture of the dehydro compound (3.0 g.), *iso*propyl alcohol (25 c.c.) and aluminium *iso*propoxide (2.0 g.) under a short still-head designed to remove acetone. In about five minutes the reduction was complete as the yellow colour of the solution completely disappeared. After removing the alcohol, the residue was acidified and the solid (3 g.) was collected and crystallised from alcohol in prismatic needles (2.6 g.), m.p. 169-70°. On working up the mother-liquor a further quantity of the material was obtained.

(*ii*). *With Sodium or Potassium Borohydride*.—A suspension of the dehydro compound in methanol (dry, 40 c.c.) (I, 4.1 g.) was stirred and treated with potassium or sodium borohydride (0.6 g.), added in small portions. Soon after the reduction was complete, colorless crystals (2.1 g.) of (A), m.p. 167°, began to separate. This was collected and the filtrate concentrated and precipitated with water. The resulting solid was dried and dissolved in a minimum quantity of alcohol and left overnight. The crystals deposited were a mixture of hard lumps (m.p. 167°) and fine plates (B, m.p. 144°), separable mechanically. A better separation was effected by warming the mixture carefully till the plates went just into solution, leaving the lumps and then filtering quickly. The filtrate deposited crystals of the *alcohol* (II) (B, 0.36 g.). (Found: C, 83.4; H, 5.4. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.5%). A further quantity was obtained with difficulty by working up the mother-liquor. The compound dissolved in sulphuric acid with an orange-yellow solution, exhibiting a strong green fluorescence. *I. R. spectrum*: Bands at 6.02 M, 6.13 M, 6.99 S, 7.33 S, 8.07 M, 8.42 M, 10.08 M, 10.56 M, 11.61 M, 11.89 M, 12.14 M and 12.55 Sμ. The compound gave methane with methylmagnesium iodide.

(*iii*). *With Lithium Aluminium Hydride-Aluminium Chloride*.—The dehydro compound (1.0 g.) was added gradually to a stirred solution of $LiAlH_4$ (0.42 g.) in ether (20 c.c.) to which a solution of freshly sublimed aluminium chloride (2.2 g.) in ether (20 c.c.) had been previously added with usual precautions.

* All m.p. s. are uncorrected.

The mixture was stirred for 2 hours, decomposed with moist ether, acidified with sulphuric acid, the ethereal solution separated and washed with alkali. The alkaline layer on acidification furnished *bis*(2-hydroxy-1-naphthyl)-methane (III) (0.8 g.), m.p. and mixed m.p. 201°. The neutral matter (0.095 g.) was found to contain solely the unsaturated alcohol (A), m.p. 166-67°; a meticulous search did not reveal the presence of any other compound.

*Potassium Borohydride Reduction of 3″-Bromo-dehydro-*bis*(2-hydroxy-1-naphthyl)-methane.*—A suspension of the compound (0.1 g.) in methanol (2 c.c.) was stirred and potassium borohydride (0.04 g.) added. The resulting colorless solution was concentrated and precipitated with water. The alkali-insoluble, colorless material (m.p. 168-200°) was a mixture of stereoisomerides which on several crystallisations from alcohol gave one *isomer*, m.p. 200°, in pure condition. (Found: C, 66.8; H, 5.1. $C_{21}H_{15}O_2Br$ requires C, 66.5; H, 5.1%).

On oxidation with manganease dioxide in chloroform (*vide infra*), the dehydro compound, m.p. and mixed m.p. 136°, was obtained back.

Manganese Dioxide Oxidation of (II).—Both the epimeric alcohols (0.1 g.) in chloroform (5 c.c.) were oxidised by refluxing with manganese dioxide (good quality, 1.0 g.) for 5 minutes and then filtered. The yellow filtrate was concentrated and the residue in each case crystallised from acetic acid, affording (I), m.p. 170°, undepressed on admixture with an authentic specimen.

Oppenauer Oxidation of (II).—The unsaturated alcohol (A) or a mixture of (A) and (B) (as obtained in borohydride reduction) (0.5 g.) was dissolved in dry benzene (20 c.c.) and then refluxed for 5 hours after addition of pure aluminium *iso*propoxide (0.5 g.) and benzoquinone (pure, 2.5 g.) when a deep blue precipitate separated. The mixture was then acidified, the organic matter taken up in ether, filtered, washed several times with alkali and then the solvent removed. The residue (0.45 g.) solidified in contact with alcohol and crystallised from acetic acid in yellow plates, m.p. 170°, identical with the dehydro compound (I).

Action of Acid on (II).—The compound (A, 0.5 g.) was dissolved in acetic acid (4 c.c.) and boiled for 5 minutes after addition of a few drops of HCl (conc.). The product was taken up in ether and extracted with alkali. The alkaline solution on acidification afforded *bis*(2-hydroxy-1-naphthyl)-methane, m.p. 201°, from acetic acid. (Found: C, 83.7, 83.8; H, 5.5, 5.6. Calc. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.5%).

The acetyl derivative crystallised from alcohol in colorless needles, m.p. 213° (lit. m.p. 213°). The neutral ethereal solution gave a yellowish material which crystallised from acetic acid in yellowish plates, m.p. 203-204° and identified as the dibenzoxanthene (IV), m.p. 203-204°. (Found: C, 89.0; H, 4.9. Calc. for $C_{21}H_{14}O$: C, 89.4; H, 4.9%).

Catalytic Reduction of (II).—The compound (A, 0.5 g.) was hydrogenated in acetic acid (5 c.c.) with the aid of pre-reduced palladised charcoal (0.2 g., 30%). One molecular proportion of hydrogen was absorbed in 10 minutes. On working up

the *product* was obtained in prismatic needles (0.4 g.), m.p. 118°. (Found: C, 83.4; H, 5.9. $C_{21}H_{18}O_2$ requires C, 83.4; H, 5.9%). On keeping in alcoholic solution or even in the solid state, the melting point slowly rose to that of the stable epimeride, m.p. 153° (*vide infra*). The benzoyl derivative, prepared in pyridine solution, was obtained as hard prisms, m.p. 138.5°, identical with benzoyl derivative of its epimeride. (Found: C, 82.6; H, 5.4. Calc. for $C_{28}H_{22}O_3$: C, 82.7; H, 5.4%). On hydrolysis with alkali the stable epimer, mentioned above, was obtained, m.p. 153°, after several crystallisations.

The compound (B) on similar hydrogenation quickly absorbed one mole of hydrogen and the product crystallised from alcohol in colorless leaflets, m.p. 153°; the mixed m.p. with the unstable isomer (m.p. 118°) was 135°, clearing at 138° and the mixed m.p. with the catalytic hydrogenation product (m.p. 143-45°) (Chatterjea, *loc. cit.*) was 149°, clearing at 152°. (Found: C, 83.5; H, 6.0. Calc. for $C_{21}H_{18}O_2$: C, 83.4; H, 5.9%).

The author wishes to thank the Ministry of Education, Govt. of India for a generous grant. Thanks are also due to Principal M. Q. Doja and Profs. P. C. Sinha and B. P. Gyani for facilities. The U.V. absorption data were obtained through the courtesy of Prof. P. C. Dutta of the Indian Association for the Cultivation of Science, Jadavpur, and the I. R. spectra were taken at the National Chemical Laboratory, Poona.

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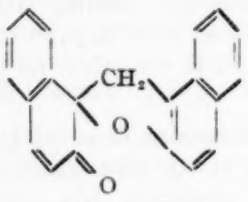
PHENOLIC OXIDATION. PART III. STRUCTURE OF ABEL'S ABNORMAL OXIME

BY J. N. CHATTERJEA

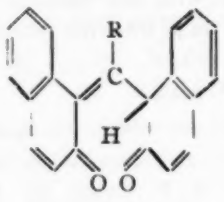
Dischendorfer's supposed identification of an abnormal oxime, isolated by Abel from dehydro-*bis* (2-hydroxy-1 naphthyl)-methane with 3:4-6:7-dibenzoacridone, has now been disproved by a direct synthesis of the latter. Alternative structures for the 'oxime' have been discussed.

In previous papers evidence was put forward and discussed in support of the structure (I) for dehydro-*bis*(2-hydroxy-1-naphthyl)-methane (Chatterjea, this *Journal*, 1950, **27**, 375; 1958, **35**, 37; cf. Pummerer and Cherbuliez, *Ber.*, 1914, **47**, 3477; Shearing and Smiles, *J. Chem. Soc.*, 1937, 1931). A second structure (II, R=H), advanced originally by Kohn and Ostersetzer (*Monatsh.*, 1918, **39**, 299), was specially supported by Dischendorfer (*Ber.*, 1926, **59**, 774) who supposed that an 'abnormal oxime' $C_{21}H_{13}NO$ (oxime

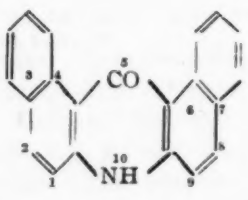
minus one mol. of water), normally isolated from (I) by Abel (*Ber.*, 1892, **25**, 3477), was the dibenzoacridone (III) and explained its formation by supposing that the normal oxime derived from (II : R=H) rearranged, the oxygen migrating from nitrogen to the central carbon atom, furnishing (IV) as an intermediate which passed into (III) with the elimination of a molecule of water. The yellow colour of the 'abnormal oxime', its high melting point, its solubility in alcoholic alkali and the isolation di-β-naphthylamine from it by zinc dust distillation led Dischendorfer to suppose its identity with (III) ; his conception gained support from his observation that (II : R=Ph) in which hydrogen atom was not attached to the central carbon atom did afford a normal oxime.



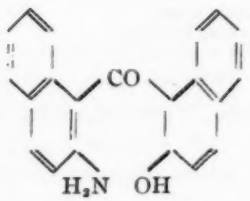
(I)



(II)



(III)

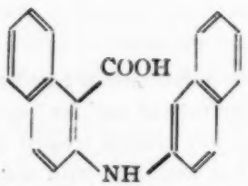


(IV)

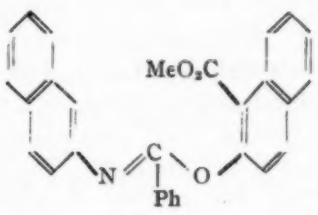
It may, however, be pointed out that the internal oxidation-reduction, as postulated by Dischendorfer, is without any known analogy. Further, the compound (II : R=Ph) cannot yield any acridone, if at all, for ≡C.Ph part of the molecule will have to be changed into >C=O and the severity of zinc dust distillation also makes its precise significance in respect of the compound's structure rather doubtful. A direct synthesis of (III) was therefore felt very desirable.

2-Chloro-1-naphthoic acid was condensed with β-naphthylamine in the presence of copper in amyl alcohol, affording the intermediate (V). The yield was only 1-2% ; efforts to raise it under various conditions were unsuccessful on account of the tendency of formation of various byproducts and, in agreement, Cymerman-Craig and Loder (*J. Chem. Soc.*, 1955, 4309) reported that the Ullmann condensation of 1-bromo-2-naphthoic acid with α-naphthylamine yielded only 2-naphthoic acid. Further work with the acid (V) was not possible. Finally, methyl 2-hydroxynaphthalene-1-carboxylate (new preparation) was condensed with *N*-β-naphthylbenzimidoyl chloride, giving rise to

to the ether (VI), which smoothly underwent the Chapmann rearrangement (*ibid.*, 1927, 1743 ; Jamison and Turner, *ibid.*, 1937, 1954 ; Cymerman-Craig and Loder, *loc. cit.*), affording the acridone (III) in good yield. The product was clearly *different* from Abel's oxime.

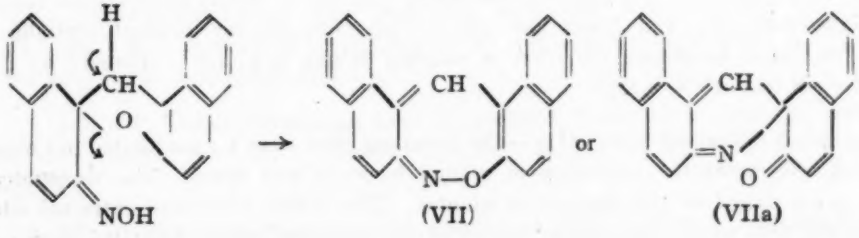


(V)



(VI)

The 'oxime' has now been briefly examined. This compound is very stable and can be sublimed. It is non-basic, contains no active hydrogen and is reduced by zinc-acetic acid or by catalytic hydrogenation (Adams' catalyst) or lithium aluminium hydride to a colorless dihydro derivative. The latter contains an active hydrogen but could not be acylated. The presence of quinonoid nucleus is strongly suggestive and the expressions (VII) or (VIIa) are provisionally advanced for this compound (cf. Kohn *et al.*, *loc cit.*) Of these, (VII) is preferred on chemical grounds although the infra-red analysis favours the expression (VIIa). The I. R. spectra of the oxime and its dihydro derivative had many features in common. The relevant bands of the former are at 6.02 μM (α-β-unstaturated ketone), 6.17 μM (=C=N−) and that of the reduced product at 5.98 μS (α-β-unsaturated ketone), 6.33 μS (NH deformation) and an absence of hydroxyl band. The oxime also formed an ether-soluble complex with methylmagnesium iodide and could be recovered *unchanged* from it. This is indicative of an initial complex formation at a tertiary nitrogen atom and also disposes of the possibility of the expression (VIIa) for the compound.



(VII) (VIIa)

The 3″-bromo derivative of (I) (Shearing and Smiles, *loc. cit.*) did not form any oxime ; on oximation it afforded either amorphous or unchanged compound.

During this work several 9-arylxanthenes were prepared by the action of aromatic aldehydes on 2-naphthol.

EXPERIMENTAL

2-Chloro-1-naphthoic Acid (cf. Rabe, *Ber.*, 1889, **22**, 394).—A mixture of 2-hydroxy-1-naphthoic acid (5.0 g.) and PCl_5 (12.0 g.) was heated in a sealed tube at 190° for 8 hours. The resulting liquid mass was allowed to evaporate and the oily residue treated with water and left overnight. The dirty solid that separated was extracted with sodium carbonate and acidified to afford the chloro-acid which crystallised from water (charcoal) in colorless prismatic needles, m.p. 155-57° (lit. m.p. 152-53°); yield 1.2 g.

Condensation of 2-Chloro-1-naphthoic Acid with β-Naphthylamine.—A mixture of the above chloro-acid (0.6 g.), β-naphthylamine (0.42 g.), dry potassium carbonate (0.5 g.), freshly precipitated copper (15 mg.) and amyl alcohol (3 c.c.) was refluxed in an oil-bath for 4 hours. The solution soon turned purple and the reaction mixture was poured into water; amyl alcohol and β-naphthylamine were removed by steam-distillation. The aqueous solution was filtered from the blue residue and acidified, when a yellow gummy precipitate was obtained. The *acid* (V) crystallised from alcohol in pale yellowish prisms, m.p. 153° (evolution of gas); the melt solidified and remelted at 169-70° (corresponding to the m.p. of di-β-naphthylamine). (Found: N, 4.0. $C_{21}H_{15}O_2N$ requires N, 4.4%). The melt was insoluble in alkali.

Methyl 2-hydroxynaphthalene-1-carboxylate was prepared in an excellent yield and purity by the action of one molecular proportion of diazomethane on an ethereal solution of 2-hydroxy-1 naphthoic acid. On working up in the usual manner, the ester was obtained as colorless needles, m.p. 80° (Schmitt and Burkard, *Ber.*, 1887, **20**, 2702, report m.p. 76°).

1-Methoxycarbonyl-2-naphthyl-N-β-naphthylbenzimidate (VI) was prepared from the foregoing ester and *N*-β-naphthylbenzimidoyl chloride by closely following the recipe of Cymerman-Craig and Loder (*loc. cit.*). The crude gummy product crytsallised from methanol, furnishing the *ether* in colorless prisms, m.p. 108°. (Found: N, 3.1. $C_{29}H_{21}O_2N$ requires N, 3.2%).

3:4-6:7-Dibenzoacridone (III).—The foregoing ether (0.15 g.) was heated in a metal bath at 280° when the formation of methyl benzoate was noted. The temperature was slowly raised to 320° during 15 minutes. The cooled mass was extracted with hot acetic acid when straw-yellow plates of the *dibenzoacridone* separated (0.08 g.), m.p. 308-309°; mixed m.p. with Abel's oxime (m.p. 360°) was 285-95°. (Found: C, 85.2; H, 4.5; N, 4.7. $C_{21}H_{13}ON$ requires C, 85.4; H, 4.4; N, 4.7%). The compound dissolved in sulphuric acid with a light yellow solution, exhibiting a strong violet fluorescence.

Abel's Oxime.—This was prepared according to Dischendorfer (*loc. cit.*). On treating this compound with methylmagnesium iodide (excess), no gas was evolved; the material passed into an orange solution and gradually an orange complex separated. The orange solution was filtered under nitrogen, acidified, ether removed and the resulting yellow compound was identified as the original material. On fusion with potassium hydroxide, traces of a primary amine (diazo coupling test) along with unchanged material were obtained. *I. R. spectrum*: Bands at 6.02 M, 6.17 M, 7.32 M, 7.64 M, 7.91 M, 8.25 M, 9.32 M, 10.38 M, 10.74 M, 11.90 M, 12.31 M, 12.48 Sμ.

Reduction of the 'Oxime'.—(*a*). A suspension of the compound (1.5 g.) in boiling acetic acid (50 c.c.) was treated with zinc dust (5 g.) till the yellow particles disappeared ($\frac{1}{2}$ hour); the mixture was filtered and added to water. The precipitated mass crystallised from acetic acid in colorless plates (0.6 g.), m.p. 322-24° (decomp). (Found: C, 84.5; H, 5.2. $C_{21}H_{13}ON$ requires C, 84.8; H, 5.0%). The compound dissolved in H_2SO_4 with an orange colour, turning yellow and finally greenish. The compound liberated methane with methylmagnesium iodide and could be recovered back from the resulting ethereal solution. On attempted acetylation with acetic anhydride—pyridine, the original material was obtained. Attempts to oxidise the compound to the 'oxime' with ferric chloride were unsuccessful. *I. R. spectrum*: Bands at 5.98 S, 6.33 S, 7.05 S, 7.32 S, 9.32 M, 10.35 M, 10.69 M, 11.05 M, 11.59M and 12.48 Sμ.

(*b*). A suspension of the 'oxime' (0.5 g.) in acetic acid (30 c.c.) was hydrogenated at the room temperature and atmospheric pressure with Adams' catalyst (0.1 g.) for 24 hours. A mixture of the unchanged compound and the dihydro derivative (m.p. 322-24°, yield 30%) was obtained and separated by crystallisation from acetic acid.

(*c*). On treating an ethereal suspension of the compound (0 5 g.) with lithium aluminium hydride (0.3 g.), the crystals turned orange but gradually went into solution (12 hours) at the room temperature. On working up, a small quantity (*ca.* 0.15 g.) of the dihydro compound, m.p. 322-23°, was obtained.

The reduction could not be brought about by sodium borohydride in methanol.

9-*Aryldibenzoxanthenes.*—The following xanthenes were prepared by adding HCl (conc.) to a mixture of β-naphthol (2 *M*) and appropriate aromatic aldehyde in acetic acid at the room temperature.

1 : 2-7 : 8-*Dibenzo*-9-p-*toluylxanthene* crystallised from acetic acid in colorless glistening plates, m.p. 231°. (Found: C, 90.6; H, 5.5. $C_{28}H_{20}O$ requires C, 90.4; H, 5.4%).

1 : 2-7 : 8-*Dibenzo*-9-p-*anisylxanthene* crystallised from butanol in colorless shining leaflets, m.p. 208°. (Found: C, 86.0; H, 5.2. $C_{28}H_{20}O_2$ requires C, 86.6; H, 5.1%).

1 : 2-7 : 8-*Dibeznzo*-9-p-*nitrophenylxanthene* crystallised from butanol in yellowish plates, m.p. 290°. (Found: C, 80.3; H, 4.2. $C_{27}H_{17}O_3N$ requires C, 80.4; H, 4.1%).

1 : 2-7 : 8-*Dibenzo*-9-α-*naphthylxanthene* crystallised from a large volume of acetic acid in thick plates, m.p. 240°. (Found : C, 90.7 ; H, 5.2. $C_{31}H_{20}O$ requires C, 91.2 ; H, 4.9%).

The author wishes to record his grateful thanks to the Ministry of Education, Govt. of India for a generous grant. Thanks are also due to Principal M. Q. Doja and Prof. B. P. Gyani for facilities. The I. R. spectra were determined at the National Chemical Laboratory, Poona.

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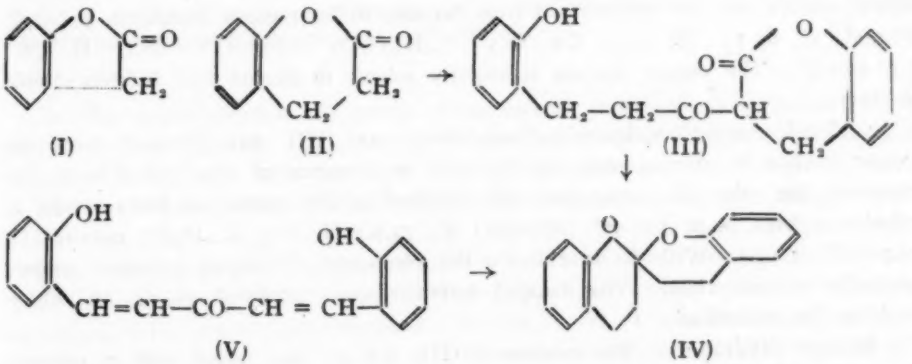
SELF-CONDENSATION OF 3:4-DIHYDROCOUMARIN

By J. N. Chatterjea

Dihydrocoumarin is shown to undergo self-condensation with the aid of sodium hydride, and the product has been converted into *bis*(2:2′)-*spiro*-chroman.

*iso*Coumaranone (I) has been shown to undergo self-condensation with the aid of sodium alkoxides or better sodium hydride, affording 3-*o*-hydroxyphenylacetylcoumaranone-2 (Chatterjea, this *Journal*, 1956, **33**, 175; Geissman and Armen, *J. Amer. Chem. Soc.*, 1955, **77**, 1623). It was of interest to extend the reaction to the ring homologue, 3:4-dihydrocoumarin (II). Indeed, dihydrocoumarin underwent self-condensation with the aid of sodium hydride, yielding dimer, $C_{18}H_{16}O_4$, isolated through the copper chelate, together with a small quantity of a neutral compound, $C_{17}H_{16}O_2$, which was formed in a substantial quantity when an excess of the hydride was employed.



The self-condensation product is assigned the structure (III) (analogous to the self-condensation product of *iso*coumaranone) on account of the following facts: (*i*) the compound is phenolic, (*ii*) it shows a typical ferric reaction and as mentioned above, it affords a copper chelate, and (*iii*) on hydrolysis with acid the compound loses a molecule of carbon dioxide, forming a neutral compound, identical with the above mentioned compound, $C_{17}H_{16}O_2$ which, on the basis of the structure (III) for the self-condensation product, should be (IV) and indeed proved identical with an authentic specimen of spiran *bis*(2:2′)-*spiro*-chroman, previously prepared by Borsche (*Ber.*, 1912, **45**, 46) by the catalytic reduction of *bis*(*o*-hydroxybenzylidene)-acetone (V).

Dihydrocoumarin is much less reactive than *iso*coumaranone. Attempts to acylate the compound with sodium acetate-acetic anhydride under vigorous conditions afforded unchanged product (cf. Chatterjea, *loc. cit.*).

*EXPERIMENTAL

3:4-Dihydrocoumarin was prepared by the catalytic reduction of coumarin in acetic acid in the presence of palladised charcoal or palladised barium sulphate (5%) at atmospheric pressure. The absorption of hydrogen was very rapid and the yield was nearly quantitative.

Self-condensation of Dihydrocoumarin.—Dihydrocoumarin (2.2 g.) was added to a suspension of an excess of sodium hydride (0.45 g.) in benzene (15 c.c.) and the mixture refluxed under nitrogen for 3 hours with usual precautions to exclude moisture. Hydrogen was evolved and a white precipitate separated. Excess of the hydride was eliminated with alcohol ; ice-water was added and the alkaline layer drawn off, acidified and extracted with ether ; the ether was removed and the residue left in contact with acetic acid. Colorless crystals of (IV) separating were crystallised from acetic acid in colorless needles, m. p. 107°, yield 0 3 g. (Found : C, 80.9, 80.9 ; H, 5.6, 5.9. Calc. for $C_{17}H_{16}O_2$: C, 80.9 ; H, 6.2%).

The compound is insoluble in boiling alkali and shows no ferric reaction. The filtrate was brought to p_H 7, extracted with ether (40 c.c.) and the ether solution shaken with a saturated solution of copper acetate for 1 hour. After removal of ether, the sludge of crystals was filtered, washed with alcohol and the greenish *copper chelate* (0.23 g.) crystallised from benzene in light green plates, m. p. 217°. (Found : C, 65.5 ; H, 5.0 ; Cu, 10.5. $C_{36}H_{30}O_8Cu$ requires C, 66.1 ; H, 4.6 ; Cu, 10.0%). The copper chelate is slightly soluble in alcohol and is fairly soluble in ether.

3-[β-(o-Hydroxyphenyl)propionyl]-chroman-2-one (III) was liberated from the copper chelate by stirring with H_2SO_4 (dil.) in presence of ether for ½ hour. On removing the ether the *compound* was obtained which crystallised from alcohol in colorless prisms, m.p. 150-51°. (Found : C, 72.5 ; H, 5.1. $C_{18}H_{16}O_2$ requires C, 72.9 ; H, 5.4%). With ferric chloride the compound developed a yellow colour, gradually turning violet. The diacetyl derivative was obtained as an oil which could not be crystallised.

Ketonic Hydrolysis.—The compound (III, 0.1 g.) was boiled with a mixture of acetic acid (1.5 c.c.) and HCl (conc., 1 c.c.) for 2 hours. Evolution of carbon dioxide took place and the resulting oil which solidified crystallised from alcohol in colorless leaflets, m.p. 107°, identical (mixed m p.) with an authentic specimen of *bis(2 : 2')-spiro*-chroman. Borsche (*loc. cit.*) reported m.p. 110° for the compound ; prepared according to Borsche's method by the hydrogenation of (V) with palladised charcoal, the compound had m.p. 107° after vacuum distillation and crystallisation from alcohol. The compound had no absorption (in alcohol) in U. V. region.

The author is grateful to Principal M. Q. Doja for his interest in the work.

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*All m.p. s' are uncorrected.

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STUDIES ON THE NATURE OF THE RACEMIC MODIFICATIONS OF OPTICALLY ACTIVE COMPOUNDS IN THE SOLID STATE. PART XIV. METHYL, ETHYL, PHENYL, *o*- & *p*-TOLYL AND α- & β-NAPHTHYL CAMPHOR-β-SULPHONATES (*d*- & *dl*-)

By Bawa Kartar Singh and S. Ramagopala Sarma

The nature of the racemic forms of methyl, ethyl, phenyl, *o*- and *p*-tolyl, and α- and β-naphthyl camphor-β-sulphonates has been studied with the aid of melting point-compositon diagrams. It is found that the racemic modifications of esters, namely, methyl, ethyl, *o*-tolyl, phenyl, *p*-tolyl and α-naphthyl camphor-β-sulphonates are *dl*-compounds, whereas the racemic form of β-naphthyl camphor-β-sulphonate exists as a solid solution.

In this communication the nature of the racemic modifications of methyl, ethyl, phenyl, *o*- and *p*-tolyl, and α- and β-naphthyl camphor-β-sulphonates has been studied. Out of the three methods described (Roozeboom, *Ber.*, 1899, **32**, 537; *Z. physikal. Chem.*, 1899, **28**, 494; Bruni, *Gazzetta*, 1900, **30**, 35; Singh, B.K. *et al.*, *Proc. Nat. Acad. Sci. India*, 1944, **14**, 171), the one based on Roozeboom's freezing (melting) point-composition diagrams has been employed to diagnose the nature of the racemic modifications. If the diagram is composed of (*i*) three curves, the racemic form is a true *dl-compound*; (*ii*) two curves, it is a *mechanical mixture* or *conglomerate*; (*iii*) one curve, a *solid solution* of the optically active and opposite forms.

We have characterised the racemic form of β-naphthyl camphor-β-sulphonate as a *solid solution* and the racemic forms of the rest of the substances studied as *dl-compounds*. As the diagrams are symmetrical, only one of the active forms is required for the study.

Experimental

All the racemic esters as well as *p*-tolyl *d*-camphor-β-sulphonate are new substances. Methyl, ethyl, phenyl, *o*-tolyl, α- and β-naphthyl esters of *d*-camphor-β-sulphonic acid were prepared according to Hilditch and Edmindson (*J. Chem. Soc.*, 1910, **97**, 220).

The aryl esters of camphor-β-sulphonic acids (*d*- and *dl*-) were prepared by the Schötten-Baumann reaction. Camphor-β-sulphonyl chloride (slightly in excess of one mol. proportion) was added to a solution of phenol or naphthol (one mol.) in dilute sodium hydroxide solution (10%), maintained at 85-90°, so as to keep the sulphonyl chloride in molten condition. The mixture was shaken well for 15 minutes, cooled, filtered and recrystallised from rectified spirit. *m*-Tolyl *d*-camphor-β-sulphonate could not be isolated, as it formed a gummy mass; its racemic form (m.p. 89°), however, could be prepared (Table I).

The alkyl esters were prepared by a somewhat different method. The solution of camphor-β-sulphonyl chloride (one mol.) in methyl or ethyl alcohol was added to the cooled solution of sodium alkoxide (one mol.). When the reaction was complete after 15 minutes, the mixture was poured on ice, the separated ester filtered and crystallised from the corresponding alcohol.

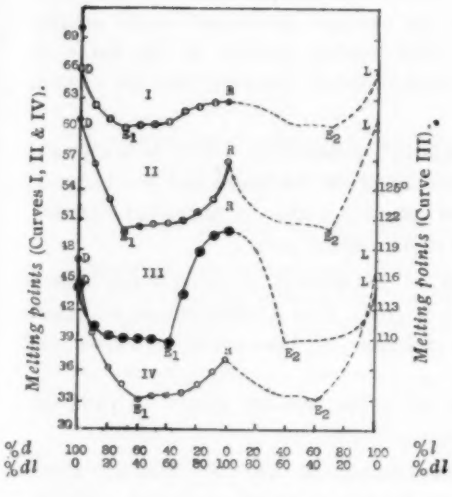
The physical properties and the results of analyses of different esters are recorded in Table I.

TABLE I

Esters of camphor-β-sulphonic acid & mol. formula.		M.P.	Crystalline form.	% Sulphur. Found.	Calc.	Remarks.
Methyl $C_{11}H_{18}SO_3$	*d*-	61°	Thin plates	12.65	13.01	A. Solubility:-All the compounds are fairly soluble in ether, benzene, ethyl acetate, pyridine, chloroform, and methyl alcohol; less so in ethyl alcohol and insoluble in water.
	dl-	57°	Do	13.27		
Ethyl $C_{12}H_{20}SO_3$	*d*-	47°	Do	12.36	12.26	
	dl-	37°	Do	12.06		
Phenyl $C_{16}H_{20}SO_3$	*d*-	38°	Rectangular prisms	10.97	10.97	
	dl-	53°	Prismatic needles	10.84		
o-Tolyl $C_{17}H_{22}SO_3$	*d*-	58°	Needles	10.67	10.46	B. Melting points: The melting point of phenyl *d*-camphor-β-sulphonate, as reported by Hilditch*, is 48°, whereas we find it to be 38°. Similarly α-naphthyl *d*-camphor-β-sulphonate melts at 115°, whereas, it was reported** to melt at 109°.
	dl-	87°	Rectangular cubes	10.31		
m-Tolyl $C_{17}H_{22}SO_3$	*d*-		Gummy consistency			
	dl-	89°	Rectangular cubes	10.33	10.46	
p-Tolyl $C_{17}H_{22}SO_3$	*d*-	64°	Prismatic needles	10.34	10.45	
	dl-	62.5°	Do	10.14		
α-Naphthyl $C_{20}H_{22}SO_4$	*d*-	115°	Needles	8.84	8.94	*Hilditch (*J. Chem. Soc.*, 1909, **95**, 157c).
	dl-	121°	Rectangular cubes	9.06		
β-Naphthyl $C_{20}H_{22}SO_4$	*d*-	100°	Rectangular plates	9.12	8.94	**Hilditch (*ibid.*, 1909, **95**, 331).
	dl-	97°	Do	8.08		

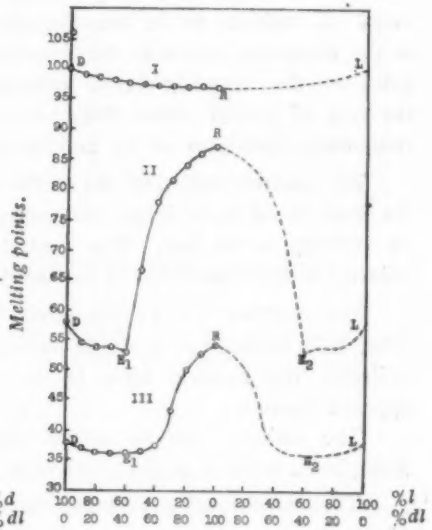
The melting point-composition diagrams (Figs. 1 and 2) were prepared as follows. The melting points of the homogeneous mixtures consisting of known proportions of *d*- and racemic forms are plotted against the percentage composition. The tables giving the melting points of the mixtures and their compositions are omitted for the sake of economy of space.

FIG. 1



Curves I to IV refer respectively to *p*-tolyl, methyl, α naphthyl and ethyl camphor-β-sulphonates.

FIG. 2



Curves I to III refer respectively to β-naphthyl *o*-tolyl and phenyl camphor-β-sulphonates.

DISCUSSION

Alkyl and Aryl Esters of Camphor-β-sulphonic Acids.—The melting point—composition diagrams (Figs. 1 and 2) of methyl, ethyl, phenyl, tolyl (*o*- and *p*-) and α-naphthyl esters consist, in each case, of three curves, DE_1, E_1RE_2 and E_2L with a central maximum, R. This indicates that the racemic esters are true *dl*-compounds. The eutectic points, E_1 and E_2, are sharp and well defined, except in the case of phenyl esters.

The *dl-d* curve of methyl esters (Fig. 1-II) is steep in the initial stages and the area under it is small, showing that the racemic ester is stable but over a small range. The *dl-d* curve of ethyl esters (Fig. 1-IV) is less steep and the area under it is smaller than that of the methyl esters. This points to the lower stability of the *dl*-ethyl ester than that of the *dl*-methyl ester.

In the case of the phenyl esters the curve, E_1RE_2, (Fig. 2-III) is steep and the area under it is large, indicating that the racemic compound is stable and the range of stability is fair. The central portion of the curve is rounded, pointing to the dissociation of the racemic compound at its melting point to the optically active components. There are no sharp and well-defined eutectic points and the curve lying in the range from 80*d*: 20*dl* to 50*d*: 50*dl* is flat and continuous, indicating the racemic modification to form solid solution with its active form in that range.

The central portion of the curve of *o*-tolyl esters (Fig. 2-II) is very steep and the area under it is very large, indicating the compound to be stable and the range of stability to be considerable. The somewhat rounded form of the curve at the maximum points to the dissociation of the racemic compound at its melting point to the optically active components. The central portion of the curve in the case of *p*-tolyl esters (Fig. 1-I) is very much rounded, showing that the racemic compound dissociates at its melting point.

The central portion of the curve of α-naphthyl esters (Fig. 1-III) is steep and the area under it is large, indicating the compound to be stable and the range of its stability to be fair. The central portion of the curve is somewhat rounded, pointing to the dissociation of the racemic form at its melting point.

The melting point-composition diagram of β-naphthyl camphor-β-sulphonates (Fig. 2-I) consists of a single continuous curve, DRL, with a minimum at R, which indicates the racemic form to be a solid solution of the optically active and opposite isomers.

The authors wish to reserve the study of other similar esters of camphor. β-sulphonic acids (*d*- & *dl*-) which is in progress.

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S-SUBSTITUTED THIOUREAS AS ANALYTICAL REAGENTS. PART II. S-METHYLTHIOUREA SULPHATE AS A REAGENT FOR SILVER

By Sushil Kumar Siddhanta and Satyendra Nath Banerjee

S-Methylthiourea sulphate has been successfully employed as a gravimetric reagent for silver. The method takes advantage of the formation of a highly insoluble, stable precipitate of silver methylmercaptide, $AgCH_3S$, which coagulates rapidly and may be filtered easily. The precipitation should be done in an ammoniacal medium. A quantitative separation of silver from zinc has also been made from a strongly ammoniacal solution containing ammonium nitrate. The precipitate of $AgCH_3S$ is less soluble than Ag_2Cl.

Siddhanta and Kundu (this *Journal*, 1955, **32**, 655) discussed the scope of using *S*-substituted thioureas as analytical reagents, and successfully employed *S*-methylthiourea sulphate as a gravimetric reagent for copper and nickel. In the present work the same reagent has been utilised in the gravimetric estimation of silver and its separation from zinc.

Klason (*Ber.*, 1887, **20** 3410) described the preparation of silver methylmercaptide. The same compound has been prepared by us as a highly insoluble precipitate in a different way by adding ammonia to a mixture of *S*-methylthiourea sulphate and silver nitrate in an aqueous solution. The precipitation is quantitative and the precipitate is stable enough to be dried at 110-25° to the stoichiometric composition of $AgCH_3S$.

A separation of silver from zinc in strong ammoniacal solution containing ammonium nitrate has also been made, as zinc is not precipitated under this condition, presumably due to the greater solubility product of $Zn(CH_3S)_2$.

The estimation of silver, if present singly, is very rapid, and takes about 1½ hours. The precipitate is highly insoluble. Moreover, the precipitate coagulates readily, permitting very easy and quick filtration. For the separation of silver from zinc, a single precipitation is sufficient.

In the estimation of silver by the usual method as silver chloride, the solubility of silver chloride in water causes a rather large error, and a correction becomes necessary. Moreover, the method is time consuming, requiring four to five hours for completion. The precipitated silver chloride is highly reactive to light, while silver methylmercaptide is not.

Experimental

Silver methylmercaptide ($AgCH_3S$) was obtained as a light yellow precipitate by mixing a solution containing an excess of *S*-methylthiourea sulphate (B.D.H.Lab. reagent)

to a hot ammoniacal solution of silver nitrate. (Found: Ag, 69.49. Calc. for $AgCH_3S$: Ag, 69.65%). Conversion factor, $AgCH_3S$: Ag = 0.6965.

Silver solutions were prepared by dissolving silver nitrate in which silver was estimated as silver chloride (Treadwell and Hall, "Analytical Chemistry", Vol. II, 1935, p. 297), applying corrections for the solubility of silver chloride in the wash liquid. Zinc solutions were prepared by dissolving zinc sulphate, in which zinc was estimated as pyrophosphate (*ibid.*, p. 146). All the above estimations were made in duplicate with exactly concordant results.

All measured volumes were taken from the same calibrated N.P.L. standard burette consistently using a float. All weighings were made by a "semi-micro balance" using a calibrated weight box.

Estimation of Silver

About two-fold excess of *S*-methylthiourea sulphate, dissolved in minimum quantity of water, was added to different measured volumes of silver nitrate solutions, each diluted to about 150 c.c. The mixture was heated just to boiling and made strongly ammoniacal (2 to 3 c.c. of 3*N* ammonia solution), when a yellowish white curdy precipitate of silver methylmercaptide was formed. The precipitate was kept at about 80° for nearly 15 to 30 minutes, filtered through a Gooch crucible (No. 3), washed with warm water and finally with alcohol and dried at 125° to a constant weight. Results are shown in Table I. The precipitation, however, was found to be incomplete at room temperature.

TABLE I

Ag taken.	Wt. of AgMeS.	Ag found.	Error.	Ag taken.	Wt. of AgMeS.	Ag found.	Error.
0.00603 g.	0.0088 g.	0.00613 g.	+0.10 mg.	0.1806 g.	0.2594 g.	0.1807 g.	+0.10 mg.
0.01206	0.0173	0.01204	−0.02	0.2408	0.3452	0.2404	−0.4
0.01809	0.0262	0.01824	+0.15	0.3010	0.4324	0.3011	+0.1
0.03618	0.0520	0.03624	+0.06	0.3612	0.5189	0.3613	+0.1
0.1204	0.1730	0.1204	±0.00	0.4816	0.6917	0.4817	+0.1

Effect of Drying Temperature and Time.—It has been observed that a constant weight of the precipitate is attained on drying at 110-25° for about 45 minutes to 1 hour. In sharp contrast to the cases of most other sulphur-containing organic reagents, the tendency of the precipitate to be oxidised by air is practically nil - even when it is heated for up to 12 hours or possibly longer at the above temperature.

Effect of Variation of Concentration of Ammonia and p_H.—It will be evident from Table II that the results are most accurate if the precipitation is made in the p_H range of 7.4 to 10.7. There is, however, a slight tendency of the precipitate for colloid formation at higher ammonia concentrations.

TABLE II

(Three-fold excess of the reagent was added)

Ag taken = 0.1204 g.

0.3*N*-Ammonia soln. added.	p_H.	Wt. of AgMeS.	Ag found.	Error.
0.5 c.c.	6.20	0.1126 g.	Large; ammonia added is insufficient to liberate the free base completely.	
1	7.44	0.1729	0.1204 g.	±0.00 mg.
2	8.93	0.1730	0.1204	±0.00
3	9.34	0.1728	0.1203	−0.1
4	9.56	0.1729	0.1204	±0.00
5	9.61	0.1728	0.1203	−0.1
10	10.70	0.1727	0.1202	−0.2
20	10.93	0.1726	0.1201	−0.3
25	11.01	0.1725	0.1201	−0.3

Effect of Keeping the Soln. after Precipitation for different lengths of Time.—From Table III it will be seen that variation of the intervals between the precipitation and filtration does not affect the result.

TABLE III

Ag taken = 0.1204 g.

Time interval (mins.) ...	5	15	30	1080
Wt. of Ag methylmercaptide (g.)	0.1732	0.1731	0.1729	0.1728
Ag found (g.)	0.1206	0.1205	0.1204	0.1203
Error (mg.)	+0.2	+0.1	±0.00	−0.1

Effect of Variation of Amount of the Reagent.—It is evident from Table IV that with the reagent not less than one and half times the amount stoichiometrically required, fairly accurate results are obtained.

TABLE IV

Ag taken = 0.1204 g. Ammonia soln. (≃0.3*N*) added = 2 c.c.

Silver : reagent (molar ratio).	Wt. of AgMeS.	Ag found.	Error.	Silver : reagent (molar ratio).	Wt. of AgMeS.	Ag. found.	Error.
1:1	0.1726 g.	0.1201 g.	−0.3 mg.	1:2	0.1729 g.	0.1204 g.	±0.00 mg.
1:1.25	0.1725	0.1201	−0.3	1:2.5	0.1730	0.1204	±0.00
1:1.5	0.1728	0.1203	−0.1	1:6	0.1729	0.1203	−0.1
1:1.75	0.1730	0.1204	±0.00				

Separation of Silver from Zinc

To a solution containing a mixture of measured volumes of silver nitrate and zinc sulphate solutions, not exceeding approximately 60 c.c. in volume, about 3 g. of ammonium nitrate and four-fold excess of the reagent were added. On diluting the solution to about 100 c.c., it was heated and approximately 10 c.c. of liquor ammonia

was added. The yellowish white precipitate of silver methylmercaptide formed was immediately filtered, washed successively with hot solutions containing 2% ammonium nitrate and 5% ammonium hydroxide, then with water, dried at 110-25° for an hour and weighed The filtrate was immediately acidified with HCl, the volume reduced to 100 c.c. by evaporation, and zinc was estimated as zinc pyrophosphate. The results are shown in Table V.

TABLE V

Ag taken.	Zn taken.	Wt. of AgMeS	Wt. of Zn. pyrophosphate.	Ag found.	Zn found.	Error (in mg.).	
						Ag.	Zn.
0.1204 g.	0.1041 g	0.1733 g.	0.2445 g	0.1207 g.	0.1049 g.	+0.3	+0.8
,,	,,	0.1732	0.2448	0.1206	0.1050	+0.2	+0.9
,,	,,	0 1737	0.2448	0.1209	0.1050	+0.5	+0.9
,,	0.0312	0.1730	0.0738	0.1204	0.0317	±0.0	+0.43
,,	,,	0.1732	0.0742	0.1206	0.0318	+0.2	+0.60
Nil	0.1041	...	0.2434	...	0.1044	...	+0.30

It is evident from the above table that the results of silver are accurate, but those for zinc are consistently about 1% high. If the weight of zinc pyrophospate be arbitrarily diminished by 1% of its value, then we may expect correct results. The consistent 1% positive error in zinc may be due to the presence of silver that has escaped precipitation as mercaptide, since with increasing alkalinity (higher ammonia cencentration) larger and larger negative errors have been noted in the estimation of silver (cf. Table II). The expected negative error in silver is absent, probably because of adsorption of some oxidation products of the thio-organic compounds which are possibly formed more rapidly in a high p_H medium.

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ANALYTICAL APPLICATIONS OF DUTOIT'S THERMOVOLUMETRY. PART II. ANALYSIS OF ZINC IN BRASS

By Kumar Krishna Chatterji

The thermometric method has been applied in the estimation of Cu and Zn by titration with $(NH_4)_2Hg(CNS)_4$. Zn in presence of Cu and in brass has been est mated using the same reagent after removing Cu from the solution as $Cu_2(CNS)_2$ by adding NH_4CNS and H_2SO_3. The method provides results for Zn which are usually + 1% higher than those obtained by gravimetric estimation as NH_4ZnPO_4.

In Part I of this series (Chatterji, this *Journal*, 1955, **32**, 366) a method for the rapid analysis of Ca and Mg in Dolomite, based on a modification of the thermometric titration of Dutoit (*J. chim. phys.*, 1922, **19**, 324, 331), was described. The same method has been extended to the analysis of brass in the present communication. Although attempt has been made to develop a quick method for the determination of both Cu and Zn in brass, it has been possible so far to apply the method for the estimation of zinc only.

Of the different reagents that were tried, $(NH_4)_2Hg(CNS)_4$ was found to suit the purpose well. This reagent affords insoluble precipitates with both Cu and Zn with sufficient heat change and is thus not specific, but it precipitates none of the other metals present in brass under the condition of the titration. The reagent has, however, one disadvantage. The precipitates of the corresponding Cu and Zn compounds appear slowly due to supersaturation phenomenon. Hence, during the thermometric titration a longer time (2 minutes) has to be allowed for attainment of a constant temperature, and the rate of stirring should also be somewhat more vigorous. For the estimation of Cu and Zn in a mixture, the following procedure was found expedient. First of all the total Cu and Zn was titrated thermometrically against a standard $(NH_4)_2Hg(CNS)_4$ solution. In an aliquot Cu was precipitated as $Cu_2(CNS)_2$ by adding NH_4CNS in presence of H_2SO_3. Zn remaining in the solution was then titrated with the same titrant, as before. It should be pointed out that the above procedure did not permit the determination of total Cu and Zn in cases (e.g. brass) where Cu : Zn ratio was wide enough. In the latter cases the corresponding thermometric diagram shows a pronounced curvature near the end-point, which could not therefore be correctly ascertained by the graphical method. However, after removal of Cu as $Cu_2(CNS)_2$, Zn could be determined with accuracy.

Experimental

The standard and stock solutions were prepared in the following way : 0.4 *M*-$(NH_4)_2Hg(CNS)_4$ solution was prepared as usual by dissolving $HgCl_2$ in NH_4SCN solution. The strengths of the prepared solutions of $ZnSO_4$ and $CuSO_4$, as obtained from the determination of Zn as $ZnNH_4PO_4$ and Cu iodometrically, were respectively 0.1042*M*

and 0.1015*M*. Zn in brass was determined according to the procedure described by Vogel ("Text Book of Quantitative Inorganic Analysis", 2nd ed., p. 559).

The thermometric apparatus is the same as that described earlier by the author (*loc. cit.*)

In the thermometric titrations of pure $CuSO_4$ and $ZnSO_4$ solutions at different concentrations (prepared by dilution of the stock solutions) 50 c.c. of the solution was taken in the Dewar. A few drops of dilute acetic acid were added, and titration was done as usual with 0.4*M*-$(NH_4)_2Hg(CNS)_4$ solution, adding 1 c.c. of the reagent at a time. As the heat change took place slowly, the rate of stirring was increased and intervals of 2 minutes were allowed between two successive additions of the titre, during which the temperature attained a constant value.

A similar procedure was employed for mixtures of Cu and Zn sulphate solutions. For the titration of Zn alone in the mixture, Cu was precipitated, as mentioned above, by adding to the mixture in the Dewar 5 c.c. of a fresh saturated solution of SO_2 in water and 10 c.c. of a 20% solution of NH_4SCN. The system was allowed to equilibriate for one hour before titration.

The following method is proposed for the thermometric estimation of Zn in a sample of brass.

About 3 g. of brass is dissolved in 30-40 c.c. of HNO_3 (1 : 1) and the solution evaporated with a few c.c. of H_2SO_4 (conc.) till HNO_3 is completely removed. The residue is taken up with water, filtered and free acid cautiously neutralised with ammonia (1 : 1). To the solution is added 10 c.c. of a 25% solution of sodium acetate, followed by 2 c.c. of glacial acetic acid, which brings the p_H of the solution around 4.0, when diluted to 250 c.c. in a volumetric flask. An aliquot of the solution (50 c.c.) is taken in the Dewar and Cu precipitated according to the procedure described above. In the residual solution Zn is titrated as before with 0.4 *M* $(NH_4)_2Hg(CNS)_4$.

The results of the thermometric titrations and those by other methods have been summarised in Tables I-IV for comparison.

TABLE I

$CuSO_4$ *with* $(NH_4)_2Hg(CNS)_4$.

	Curve a.	Curve b.	Curve c.
End-points (in c.c.)	13.0	6.55	5.25
Cu (found thermometrically in g.)	0.3307	0.1665	0.1336
Cu (found iodometrically in g.)	0.3313	0.1657	0.1325
% Error in thermometry	−0.2	+0.5	+0.8

TABLE II

$ZnSO_4$ *with* $(NH_4)_2Hg(CNS)_4$.

	Curve a.	Curve b.	Curve c.
End-points (in c.c.)	12.7	6.3	5.1
Zn (found thermometrically in g.)	0.3321	0.1654	0.1334
Zn (found gravimetrically in g.)	0.3317	0.1659	0.1327
% Error in thermometry	+0.12	−0.3	+0.54

FIG. 2

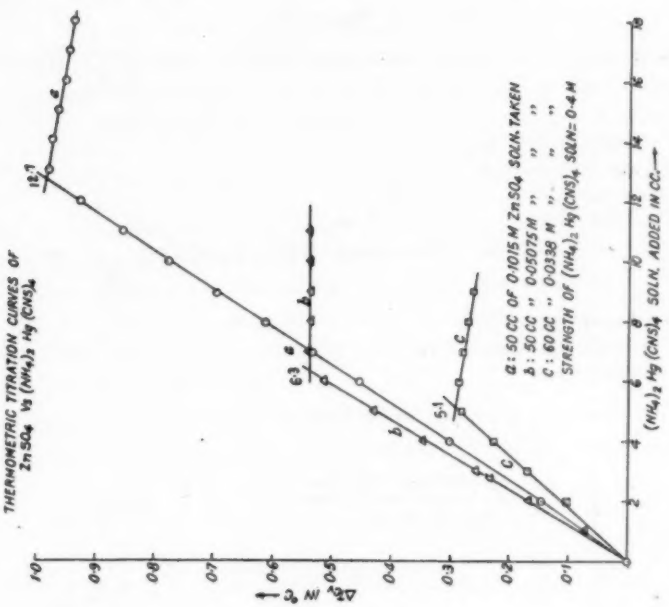

THERMOMETRIC TITRATION CURVES OF
ZnSO4 Vs (NH4)2 Hg (CNS)4
a: 50 cc of 0·1015 M ZnSO4 soln. taken
b: 50 cc " 0·05075 M " " "
c: 60 cc " 0·0338 M " " "
Strength of (NH4)2 Hg (CNS)4 soln = 0·4 M
(NH4)2 Hg (CNS)4 soln. added in cc.
ΔEv in cm

FIG. 1

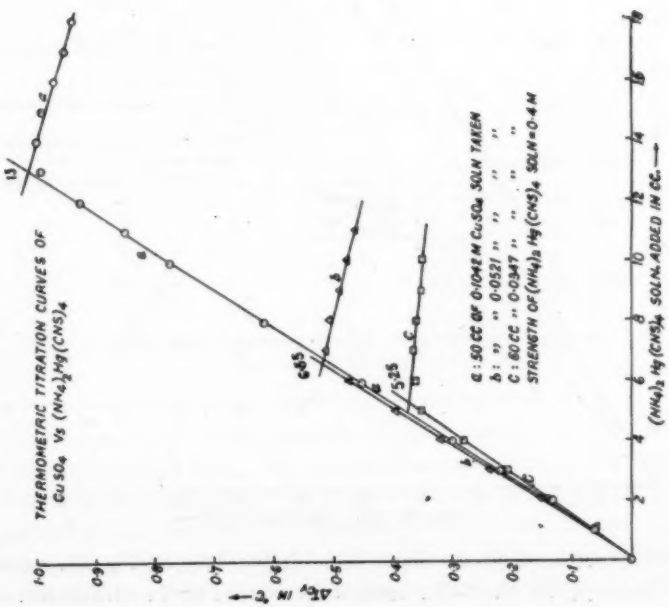

THERMOMETRIC TITRATION CURVES OF
CuSO4 Vs (NH4)2 Hg(CNS)4
a: 50 cc of 0·1042 M CuSO4 soln taken
b: " " 0·0521 " " "
c: 60 cc " 0·0347 " " "
Strength of (NH4)2 Hg(CNS)4 soln = 0·4 M
(NH4)2 Hg (CNS)4 soln. added in cc.
ΔEv in cm

TABLE III

Zn *in mixtures of* $ZnSO_4$ *and* $CuSO_4$ *solutions with* $(NH_4)_2\,Hg(CNS)_4$.

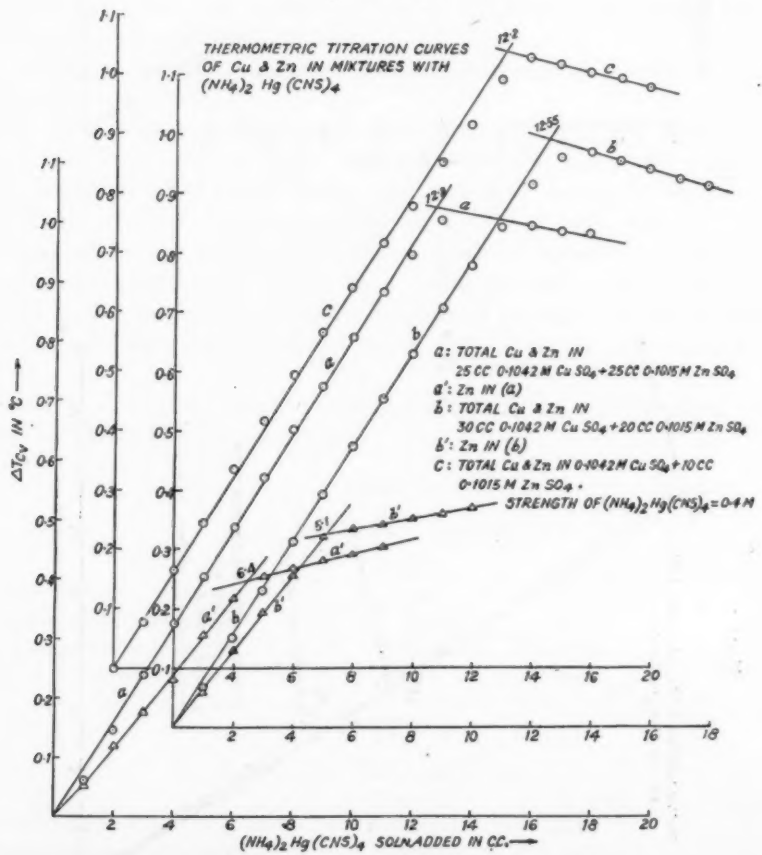
	Curve a.	Curve b.
End-points (in c c.)	6.4	5.1
Zn (found thermometrically in g.)	0.1674	0.1334
Zn (found gravimetrically in g.)	0.1659	0.1327
% Error in thermometry	+0.9	+0.54

TABLE IV

Zn *in brass with* $(NH_4)_2\,Hg(CNS)_4$.

	Curve a.	Curve b.
End-points (in c c.)	8.05	6 8
Zn (found thermetrically in g.)	35·74	30·45
Zn (found gravimetrically in g.)	35·45	30·15
% Error in thermometry	+1.0	+1.0

FIG. 3


THERMOMETRIC TITRATION CURVES OF Cu & Zn IN MIXTURES WITH (NH4)2 Hg (CNS)4
a: TOTAL Cu & Zn IN 25 CC 0·1042 M Cu SO4 + 25 CC 0·1015 M Zn SO4
a': Zn IN (a)
b: TOTAL Cu & Zn IN 30 CC 0·1042 M Cu SO4 + 20 CC 0·1015 M Zn SO4
b': Zn IN (b)
C: TOTAL Cu & Zn IN 0·1042 M Cu SO4 + 10 CC 0·1015 M Zn SO4 .
STRENGTH OF (NH4)2 Hg(CNS)4 = 0·4 M
ΔTcv IN °C
(NH4)2 Hg (CNS)4 SOLN ADDED IN CC.

The thermometric diagrams have been drawn by plotting the corrected temperatures (cf. Chatterji, *loc. cit.*) ΔT_{cv} against the volume of the titre added.

Here $$\Delta T_{cv} = \frac{\Delta T\ (V + dv)}{V}$$

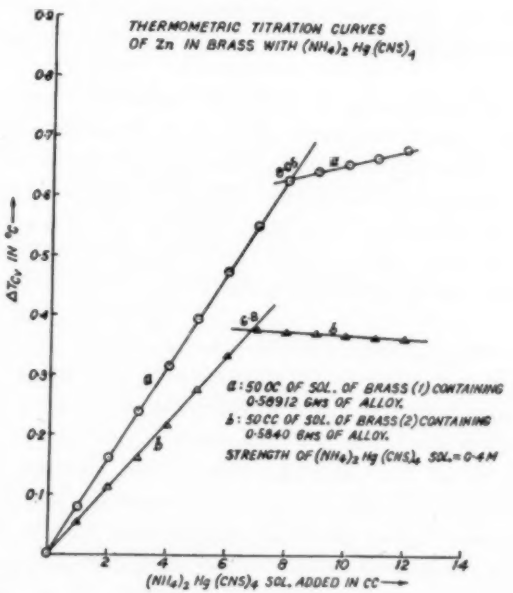
where ΔT = observed temperature change in o° arising out of the addition of dv c.c. of titre to V c.c. of the system in the Dewar.

DISCUSSION

From Tables I-IV and Figs. 1-4 it is clear that in the individual estimation of Cu and Zn and of Zn in Cu-Zn mixtures and brass, agreement is within 1% between values obtained by the thermometric and the chemical methods. The concentrations of the solutions used lie between $M/10$ and $M/30$. In the case of Zn, the thermometric method is especially recommended, as a suitable volumetric method for its estimation is still lacking.

The non-rectilinear nature of the thermometric diagram obtained in the titration of total Cu and Zn in mixtures (Fig. 3) is readily explained if we recognise the

FIG. 4


THERMOMETRIC TITRATION CURVES
OF Zn IN BRASS WITH $(NH_4)_2$ Hg (CNS)$_4$
ΔT_{cv} IN °C
$(NH_4)_2$ Hg (CNS)$_4$ SOL. ADDED IN CC
a: 50 CC OF SOL. OF BRASS (1) CONTAINING 0·58912 GMS OF ALLOY.
b: 50 CC OF SOL. OF BRASS (2) CONTAINING 0·5840 GMS OF ALLOY.
STRENGTH OF $(NH_4)_2$ Hg (CNS)$_4$ SOL. = 0·4 M

fact that during the first part of the titration of the mixture, there is coprecipitation of $ZnHg(CNS)_4$ and $CuHg(CNS)_4$, but during the later part of the operation either pure $ZnHg(CNS)_4$ or pure $CuHg(CNS)_4$ is precipitated according as Zn or Cu is present in excess in the mixture. These considerations are directly supported by the fact that as the ratios of Cu^{++} : Zn^{++} in the mixtures are varied, the resulting thermometric diagrams deviate more and more from the straight line course (Fig. 3).

The method of analysis of Zn in brass, proposed in this paper, provides results which are 1% higher than the values obtained by analysing as $Zn_2P_2O_7$. In the latter, the low result is not unlikely owing to the slight solubility of $ZnNH_4PO_4$ and consequent loss in weight during washing. Referred to the gravimetric result as the standard, the thermometric result therefore will be less by about 1%.

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REACTION BETWEEN FERRIC CHLORIDE AND AMMONIUM THIOCYANATE

By B. P. Gyani and Miss R. Misra

On subjecting ferric chloride and ammonium thiocyanate to electrolysis, cataphoresis in an agar-agar gel and diffusion through filter paper at different temperatures, the red colour is discharged around the cathode in electrolysis. The red boundary moves towards the cathode in cataphoresis. This apparent contradiction is easily understood because the red particles carry positive charges but are at the same time easily reducible. It appears from the diffusion experiments that the red particles may be colloidal in nature.

This work is in continuation of our earlier work on variation of colour in mixtures of ferric chloride and ammonium thiocyanate (this *Journal*, 1956, **33**, 160). That work was later repeated with potassium thiocyanate, and the results with ammonium thiocyanate were substantially corroborated. The variations in colour can be accounted for on the assumption that a red complex is formed in the first instance which undergoes both reduction and hydrolysis. The nature of the red complex was not investigated.

From a review of the relevant literature it appears that before more quantitative experiments are undertaken, it may be useful to clarify whether the complex is of a colloidal nature. This naturally involves qualitative experiments. We have also felt the need of repeating some older experiments, for example, those on cataphoresis, regarding which the literature appears somewhat contradictory. Thus, Schlessinger and van Valkenburg (*J. Amer. Chem. Soc.*, 1931, **53**, 1212) considered the red ion to be $Fe(CNS)_6^{3-}$, but Bent and French (*ibid.*, 1941, **63**, 568) considered it to be $Fe(CNS)^{2+}$.

It appears to be an almost universal opinion that the red substance, produced when ferric chloride reacts with a thiocyanate, is due to complex formation. According to Schwarzenburg (*Analyst*, 1955, **80**, 713) thiocyanate complexes should on the whole be mono-nuclear, soluble in water, and the complex ions should be negatively charged. The red substance has a high solubility, but the position regarding the other two properties does not appear to be quite clear. There is difference of opinion whether the red ions are positively or negatively charged, and there is no conclusive work concerning the molecular nature of the substance. A re-investigation of these aspects appears to be justified. In the experiments which follow we have studied electrolysis, cataphoresis, diffusion through a filter paper and reduction of the red substance.

Experimental

Electrolysis.—A mixture of 1% ammonium thiocyanate (20 c.c.), ferric chloride (0.0033*M*, 20 c.c.) and water (60 c.c.) was taken in a U-tube (cross-section 1.5 cm height 10 cm) and subjected to electrolysis (10-12 volts). The red colour was rapidly

discharged in the cathode compartment and after half an hour a sharp boundary, colorless/red, was formed at the bottom, with little tendency to diffuse even during several hours. The discharged liquid showed no test for ferrous ions and only a feeble indication for ferric ions. A black deposit appeared on the cathode which dissolved on treatment with HCl, or by itself if the cathode (platinum) was left in the electrolyte, but only after a long time, and responded to tests for iron. This experiment shows at first sight that the red ion may be negatively charged, thus migrating towards the anode and stripping the cathode solution almost entirely of iron, but the treatment of neutral solution with aluminium-mercury couple brings about a rapid discharge of red colour. An acidified solution is also rendered colorless when zinc is added. The discharge of colour observed may therefore be due to reduction, and the experiment does not appear conclusive.

The electrolysis in a number of acidified solutions was repeated. One of the mixtures was 20 c.c. of 0.0033*M*-$FeCl_3$, 20 c.c. of 1% ammonium thiocyanate, 55 c.c. of water and 5 c.c. of *N*-HCl, so that the mixture was $N/20$ in respect of HCl. On passing the current, the solution became distinctly hot (room temp. 29°). The rate of discharge of colour around the cathode was now much slower and there was no complete discharge of colour as in the neutral solution even after 2 hours. On stopping the current, the colour around the cathode was rapidly regained although there was a general decrease in the intensity of colour throughout the apparatus. It appeared that diffusion of red particles towards regions of lower concentration could adequately explain the observations. The observations were substantially similar when the electrolysis was made intermittent so as to minimise the heating effect. A sharp boundary was, of course, never observed in electrolysis with acidified solutions.

Cataphoresis.—To determine the charge on the red particles more definitely, we carried out a number of cataphoresis experiments. In one experiment we took a glass tube 10 cm long, bore 4-5 mm and partly filled with a warm 3% solution of agar-agar containing 5% ammonium thiocyanate. When the solution had set to a firm jelly, the top was filled with a dilute solution of ferric chloride (about 0.003*M*) and set in a beaker containing a layer of the same. Platinum electrodes were dipped in the two ferric chloride solutions. On application of a potential difference (2 volts) the sharp red boundary always moved towards the cathode irrespective of the fact whether the cathode was set at the top or bottom. The rate with which the boundary moved was not uniform, about 5 mm during the first ten minutes and about 15 mm during the next 45 minutes. The jelly warmed up due to passage of current, and one should have expected a faster rate as the experiment progressed. The heating was quite intense when the ferric chloride was acidified with HCl (about normal in the mixture) and the experiment could be continued only for a few minutes. Even then there was excessive blurring of the boundary and even a semiquantitative measurement of the rate was difficult.

Diffusion Experiments.—We hope that by observing the diffusion characteristics we would be able to judge how far the red substance may be homogeneous and also to obtain some idea about the average molecular weight. Although we did manage to have

a sharp boundary between ferric chloride and ammonium thiocyanate, it soon became blurred and a measurement of the rate of diffusion was not possible using tubes of 5 mm bore. It did not make much difference whether the ferric chloride was almost neutral or acidified with HCl. We propose to repeat these experiments using a sintered glass funnel as the diffusion cell.

We then tried a simpler technique, namely the chromatographic diffusion of the red substance through filter paper. Strips of filter paper, 0.5 cm broad, were cut, treated with the solutions shown in column 3 of Table I, and dried. One end of the strip was dipped in the experimental solutions (column 2). The rate and nature of diffusion were then visually observed. The experimental solution (2 c.c.) was taken in a test tube which was corked after inserting the paper strip to prevent evaporation. The results are set down in column 4. The first figure in column 2 stands for ferric chloride, the second for ammonium thiocyanate and the third for HCl. In some experiments one or more of these substances have been omitted.

TABLE I

Diffusion through variously treated filter paper.

No. of experiment.	Exptl. soln.	Filter paper treated with.	Observations.
1.	0.0006*M*-$FeCl_3$ 0.118 AmCNS No acid	Nil	No visible movement of a coloured boundary. A weak band observed at top after 3 days.
2.	0.0006*M*-$FeCl_3$ 0.118 AmCNS 0.10 HCl	,,	First water, then coloured boundary move up.
3.	0.592 AmCNS	0.003*M*-$FeCl_3$	Deep chocolate band in 3-4 hrs. AmCNS and rest of filter paper not coloured.
4.	0 003 $FeCl_3$	0.592*M*-AmCNS	No band at top. Slight yellow band at bottom.
5.	0 301 $FeCl_3$	0.592 ,,	Immediate chocolate band at bottom moves up rapidly. Rest of paper uniform yellow. $FeCl_3$ soln. becomes red.
6.	0.151 $FeCl_3$ 0.50 HCl	0.592 ,,	As in 5, band broader and movement quicker.
7 a.	0 06 $FeCl_3$	0 592 ,,	Neutral solutions: intensity of colour and movement of the band increase with increasing concentration of $FeCl_3$.
b.	0.120 $FeCl_3$	0.592 ,,	
c.	0.181 $FeCl_3$	0.592 ,,	
d.	0 241 $FeCl_3$	0.592 ,,	
e.	0.181 $FeCl_3$ 0.20 HCl	0.592 ,,	Acid solutions: bands broader and more diffuse and upward movement faster (20-30 minutes for reaching top).
f.	0.181 $FeCl_3$ 0.40 HCl	0.592 ,,	

These experiments were performed at room temperature, 29-31°. The experiments 7a to 7f were repeated at 12-13° (in a refrigerator). The rate of movement of the bands was then much slower than could be expected from the simple diffusion equation,

$$D = \frac{RT}{6N\pi\eta r},$$

and curiously enough very slow when acid was present. In acid solutions the bands were broader and more diffuse. The red band tended to disappear after reaching the top, more readily when acid was present. When ferric chloride alone was present in the solution (filter paper untreated), the entire strip turned yellow at a rate increasing with increasing salt concentration (12-13°). In many of the other experiments also a yellow colour persisted throughout the strip irrespective of temperature and presence of acid initially. Such a colour might be expected if ferric chloride underwent hydrolysis, for example. The yellow colour persisted for at least five days.

Discussion

It is not possible to understand all these observations at the moment, but one point appears to be substantially established. Whatever be the nature of the primary product of reaction between ferric and thiocyanate ions, the actual particles are polydisperse, and hence, perhaps colloidal in nature. The presence of acid appears to increase dispersion in favour of lower particle weights, thereby increasing diffusion. Hence, there is apparently no immediate discharge of colour around the cathode in electrolysis with acidified mixtures, since the colour lost is rapidly regained by diffusion from the rest of the solution. Any diffusing boundary which may be formed, e.g. in cataphoresis through agar-agar jelly, is naturally broad and diffuse when acid is present.

At first sight it appears difficult to understand why diffusion should be so slow through filter paper, when acid is present. However, adsorption of the red particles must take place on the cellulose before diffusion could be possible and the former is rendered unfavourable due to decreased particle weight. Perhaps presence of acid may directly produce an unfavourable electrical condition for diffusion, since the diffusing particles carry electric charges.

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STUDIES ON SEED FATS OF CUCURBITACEAE FAMILY. PART II. THE COMPONENT FATTY ACIDS OF *TRICHOSANTHES CUCUMERINA*, LINN.

By S. A. Patel, S. Bhattacharyya and M. M. Chakrabarty

The component fatty acids of *Trichosanthes cucumerina* has been investigated, using spectrophotometric and low-temperature crystallisation methods.

The seed fats of many members of the *Cucurbitaceae* family have been found to be rich in conjugated unsaturation. Compositions of the seed fats of other members of Cucurbitaceae family (Chakrabarty *et al.*, *Naturwiss.*, 1955, **42**, 344) have indicated the possibility of their use as good drying oils like Tung oil. With that end in view studies in the seed fat of *Trichosanthes cucumerina* (Bengali-Banchichinga, N.O. Cucurbitaceae), a climbing annual, grown all over India, was undertaken.

In the present investigation modern methods including spectrophotometric technique, advocated by Hilditch *et al.* (*Analyst*, 1945, **70**, 68; 1951, **76**, 899; "Chemical Constitution of Natural Fats", 3rd ed., 1956, Chapman and Hall, London) in conjunction with the low-temperature fractionation of fatty acids from organic solvents have been employed.

Fruits are oval or oblong and pointed; cells are imperfect. The fruits are from one to four inches long, and from one to one and a half inches in diameter. Till ripe, they are striated with white and green, and while ripe, they become red. Seeds are involved in a red pulp and 3/8"-1/2" size and half ellipsoidal in shape.

Experimental

The seeds were obtained from crops grown in Gujarat. The oil was extracted from ripe and dried seeds with petroleum ether (b.p. 40-60°). The characteristics of the oil and seeds are presented in Table I. The percentage of unsaponifiables was determined according to the method recommended by the American Oil Chemists' Society (Official and Tentative Methods of A.O.C.S. Method Ca- 6a- 40, 1946).

Table I

Characteristics of oil and seeds.

Seeds :	Average weight of single seed (g.)	...	0.0994
	%Yield of oil (on whole seed)	...	28.0
Oil :	Ref. index (at 40°)	...	1.4881
	%Free fatty acids (as %oleic)	...	17.0
	Sapon. equiv.	...	300.8
	I.V. (Wij's, 30 mins.)	...	134.7
	Unsaponified and unsaponifiable matters (%)	...	1.2
	%Saturated acids (Bertram's oxidation)	...	11.87

The mixed fatty acids of the oil were separated into different fractions of varying mean unsaturation by crystallising first from a mixture of ethyl ether and light petroleum ether (b.p. 40-60°) and then from acetone at -50° and -60° respectively. The details of crystallisation are shown in Chart I. Three fractions, designated A, B, C in the increasing order of iodine value, were obtained. Their proportions are shown in Table III*. The original mixed fatty acids and the fractions A, B, C were examined separately by spectrophotometric method, the details of which are presented in Table III.

Specific extinction coefficient values taken for calculation are according to Hilditch *et al.* (*loc. cit.*).

TABLE II

	Unisomerised. (268 mμ)	Alkali-isomerised. 170°/15 min. (268 mμ).	180°/60 min. (234 mμ).
α-Elaeostearic	780	1690	197
Linolenic	...	555	575
Linoleic	...	...	906

The saturated acids were determined in duplicate by Bertram's oxidation method (*Z. deut. öl-u. fett. Ind.*, 1925, **45**, 733) as modified by Palikan and Von Mikusch (*Oil & Soap*, 1938, **15**, 149) and the % oleic acid was obtained by difference.

CHART I

Low-temperature crystallisation chart.

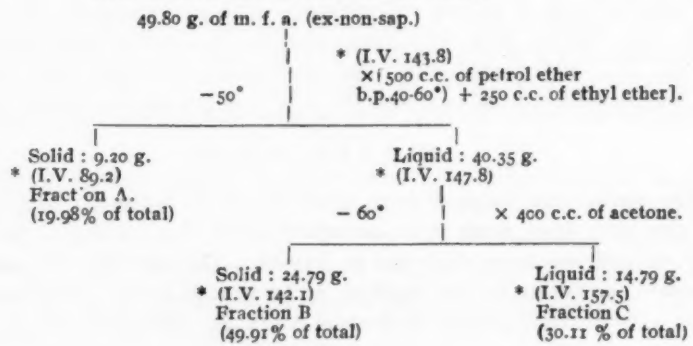

TABLE III

Spectrophotometric data.

	Iodine value.	$E^{1p.c.}_{1cm}$ at 268 mμ. Unisomerised.	$E^{1p.c.}_{1cm}$ at 268 mμ. Isomerised at 170°/15 min.	$E^{1p.c.}_{1cm}$ at 234 mμ isom. at 180°/60 min.
Mixed fatty acid	143.8	635.0	575.0	240.0
Fraction A	89.2	569.9	...	127.5
Fraction B	142.1	737.5	...	192.3
Fraction C	157.5	495.7	...	421.3

* The iodine values in these cases do not represent true iodine values because of the presence of conjugated system.

Since the oil contains tri-conjugated acid as one of the components, the iodine value is not an indication of mean unsaturation. Calculation of %oleic acid is therefore not possible from the iodine value. For this reason the %saturated acid in each fraction was determined by Bertram's oxidation method. The results are recorded in Table V along with data for component acids of different fractions.

About 7 g. of fatty acids (of I.V. nil), obtained by Bertram's oxidation method, was freed from unsponifiable matter and converted into their methyl esters. The methyl esters were fractionated in an E.H.P. column and the saponification equivalent of each fraction was determined (Table IV). The proportions of different saturated fatty acids in the total saturated acids were calculated from these data, following the method of Hilditch (*loc. cit.*), and then distributed amongst the different fractions A, B and C in the same proportion as they were present in the total. The results are shown in Table VI.

TABLE IV

Fraction No.	Wt.	S.E.	C_{16}.	C_{18}.	C_{20}.
1	1.7910 g.	275.2 g.	1.4310 g.	0.3600 g.	...
2	0.6621	285.2	0.2865	0.3756	...
3	1.0020	287.8	0.3422	0.6598	...
4	1.4220	302.6	...	1.1700	0.2520 g.
5	0.7678	325.8	...	0.0050	0.7628
Residue	1.3130	326.0	...	...	1.3130
Total ex. non sap.	6.9579	..	2.0597	2.5704	2.3278
Wt. % of ester	...	...	29.61	36.94	33.46
Wt. % of acid in sat. acid		...	29.53	37.04	33.43
			Palmitic. (C_{16})	Stearic. (C_{18})	Arachidic (C_{20})
% Acid in the whole m. f. a. (11.87 by Bertram's method)			3.51	4.4	3.96

TABLE V

Component fatty acids of different fractions.

Acids.	Fraction A. (19.98%).	Fraction B. (49.91%).	Fraction C. (30.11%).
Total saturated acids (by Bertram's method)	43.97	6.37	0.57
Palmitic	12.98	1.88	0.17
Stearic	16.29	2.36	0.21
Arachidic	14.70	2.13	0.19
Oleic (by difference)	16.91	39.69	31.14
Linoleic	7.10	12.50	40.44
Conjugated triene as α-elaeostearic	32.02	41.44	27.85

Palmitic, stearic and arachidic acids are distributed amongst the fractions A, B & C in the same proportion as in the total saturated acid.

TABLE VI

Components of different fractions (%ex N-S, in terms of total).

Acids.	A.	B.	C.	Total (% wt.)	Equiv.	Mole %.
Palmitic	2.59	0.94	0.05	3.58	0.01398	3.96
Stearic	3.25	1.18	0.06	4.49	0.01581	4.48
Arachidic	2.94	1.06	0.05	4.05	0.01298	3.68
Oleic (by diff.)	3.38	19.83	9.38	32.59	0.11200	31.71
Linoleic	1.42	6.24	12.17	19.83	0.07081	20.04
Conjugated triene as α-elaeostearic	6.40	20.67	8.39	35.46	0.12760	36.13

DISCUSSION

The seed fats of the N. O. Cucurbitaceae show two trends. In a large number of them the component acids belong to simple type, e.g. palmitic, stearic, oleic and linoleic, with saturated acids approaching 30% of total acids. In a few genera, however, presence of conjugated triene acids has been detected. Recently, this has been established with much greater accuracy. For example, *Momordica charantia, Trichosanthes anguina, Telfaria occidentalis* and others have been found to contain from 20 to 50% of conjugated triene acid. The present analysis of *T. cucumerina* seed fat has been compared with some of these in Table VII.

TABLE VII

Acids.	*M. charantia Muricata*[1].	*M. charantia* Proper[2].	*T. anguina*[3].	*T. cucumeroid*[4].	*T. occidentalis*[5].	*T. cucumerina.*
Saturated	30.47	25.90	20.70	9.0	19.0	11.87
Oleic	12.21	15.28	32.10	20.0	23.0	32.59
Linoleic	8.83	18.48	21.30	42.0	23.0	19.83
Conjugated triene acid (as α-elaeostearic)	48.49	40.34	25.90	29.0	19.0	35.46

1-3. Chakrabarty, *loc. cit.*

4. Toyama & Tuchiya, *J. Soc. Chem Ind. Japan*, 1935, **38**, 185B.

5. Hilditch & Riley, *J Soc Chem. Ind.*, 1946, **65**, 74.

It will be clear from the comparison that the seed fat of *T. cucumerina* is different from that of *T. cucumeroid*, reported by Japanese workers (*loc. cit.*), by its containing higher percentage of conjugated triene and lower percentage of linoleic acid and higher percentage of oleic, while the content of saturated acids is practically the same. The difference in composition between *T. cucumerina* fatty acids and that of another genus of *Trichosanthes*, namely *T. anguina*, reported by Chakrabarty *et al.* (*loc. cit.*), is less pronounced, and can be assumed to be the normal variation amongst the same genus. The difference in composition from the genus *Momordica* will be at once obvious from the higher percentage of saturated acids and conjugated triene acids and lower % of oleic and linoleic acids in the latter.

Another remarkable feature of the *T. cucumerina* seed fat is the presence of quite a high percentage of arachidic acid, which has hitherto not been reported in this type of fat. The presence of about 56% polyethenoid acids in the total fat, of which more than half consists of conjugated triene acid, ought to make this fat utilisable either as such or after solvent seggregation, in the surface coating industry. It is to be noted that although the conjugated triene acid has been estimated and recorded as α-elaeostearic acid, it is most likely that they are present in the form of its geometrical isomer, trichosanic acid, as shown by Ahlers *et al.* (*Chem. & Ind.*, 1954, 603 ; *Nature*, 1954, **173**, 1045) in the case of conjugated triene acids, obtained from other members of 'Cucurbitaceae' family.

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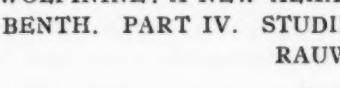
RAUWOLFININE: A NEW ALKALOID OF *RAUWOLFIA SERPENTINA* BENTH. PART IV. STUDIES ON THE CONSTITUTION OF RAUWOLFININE

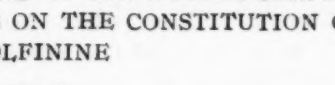
By S. Bose*

The partial structure of rauwolfinine, an indoline alkaloid (m.p. 235-36°), as reported previously, has been fully worked out and the entire structure of the base ($C_{19}H_{24}O_2N_2$) finally settled.

Rauwolfinine, an indoline alkaloid, m.p. 235-36°, occurring in *Rauwolfia serpentina* Benth. (of Dehra Dun variety) was shown to have the following partial structure (I) (Bose, this *Journal*, 1954, **31**, 47, 311, 691):



(I)



(Ia)

Further work on the constitution of rauwolfinine has been pursued and the entire structure of the base has been settled. The relevant informations are reported in the present communication.

The base, molecular formula $C_{19}H_{26}O_2N_2$ (I)of which has now been revised as $C_{19}H_{24}O_2N_2$ (Ia), does not undergo hydrogenation in presence of palladium-charcoal or Adams' catalyst and fails to react with lithium aluminium hydride. This observation implies that rauwolfinine is neither a dihydro- nor a tetrahydro-β-carboline derivative, which is in conformity with the colour reactions of the base. Obviously it is concluded that rauwolfinine is a hexahydro-β-carboline alkaloid (Ia). Acetyl, tosyl, chloro and benzoyl derivatives of the alkaloid cannot be prepared in a crystalline state. The products are always gummy, but they are found to be tetrahydro-β-carboline derivatives, as evidenced from their U.V. spectra and colour reactions

Several exploratory experiments, viz., alkali fusion, selenium dehydrogenation and dehydration etc., have been performed with a view to determining the nature of C_5H_6 (according to the new mol. formula) residue (Ia). From alkali fusion products (Bose, *loc. cit.*, p. 691) *n*-butyric, and no aromatic acid, has been isolated. The former has been characterised as its *p*-phenylphenacyl ester, m.p. 82-83°.

Selenium dehydrogenation of the base at 300° gives rise to several indolaceous products from which Ind-*N*-methylharman, m.p. 101-102°, is obtained as a major product. The same experiment, performed at 250°, yields a different base, $C_{16}H_{16}N_2$, characterisation of which has not been possible for the paucity of materials.

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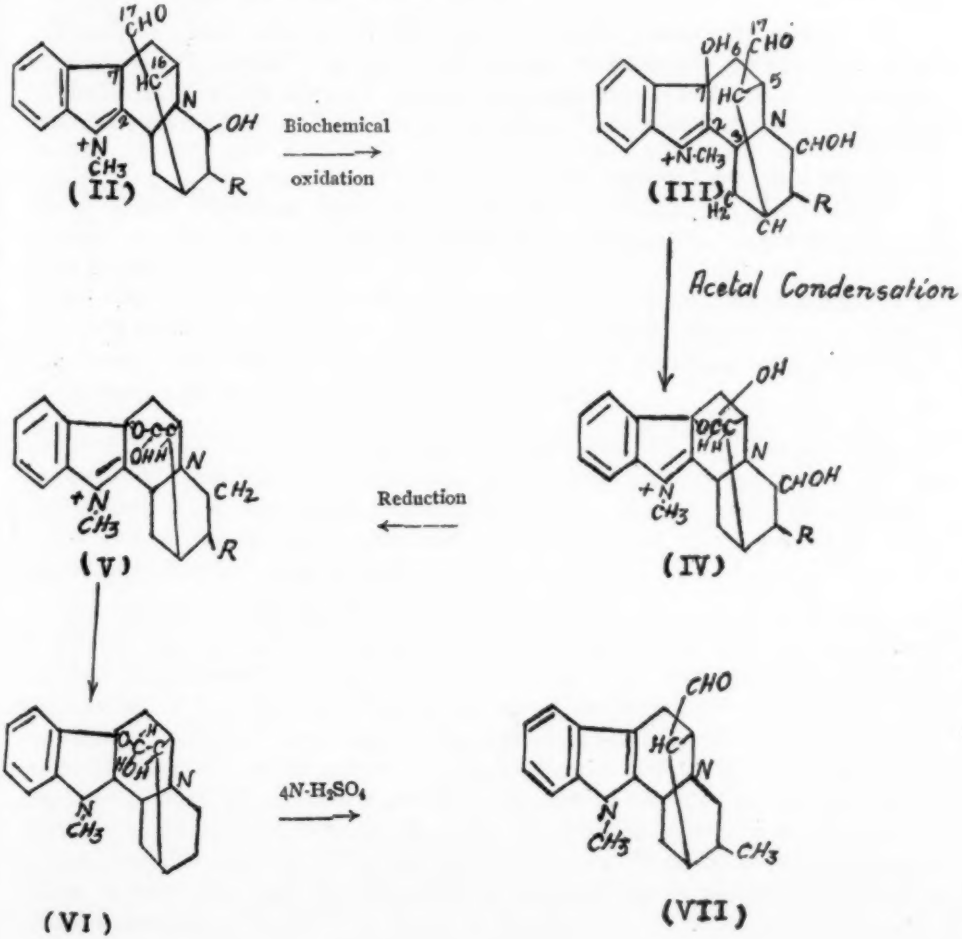
From the evidences accumulated so far, that rauwolfinine is (*i*) a hexahydro-β-carboline derivative, (*ii*) produces *n* butyric acid and no aromatic acid upon alkali fusion, (*iii*) yields only Ind-*N*-methylharman but no yobyrine, alstyrine, or its lower homologues and their derivatives during selenium dehydrogenation, and considering the fact that all Rauwolfia alkaloids are tetracyclic, it can be assessed that rauwolfinine bears a structural analogy with ajmaline (Woodward, *Angew. Chem.*, 1956, **68**, 13). These facts together with the association of rauwolfinine with ajmaline in Rauwolfia plants point out that the progenitor of these alkaloids is the same, which is shown in structure (II). Assuming Woodward's theory on the biogenesis of Rauwolfia alkaloids, as also the hypothesis on the biochemical oxidation of indole compounds developed by Witkop and Goodwin (*J. Amer. Chem. Soc.*, 1953, **75**, 3371), structural evolution of rauwolfinine from (II) has been possible, as shown below:



Thus, during the biosynthesis of rauwolfinine acetal condensation occurs at C_7-C_{17} instead of aldol, as observed in ajmaline. In ajmaline R is an ethyl, whereas in rauwolfinine (VI) it must be a methyl group as demanded by its molecular formula. Confirmation regarding the correctness of this structure (VI) follows from its behaviour towards $4N$-H_2SO_4. When warmed with this reagent, the base develops an indole chromophoric group and is converted into a tetrahydro-β-carboline compound (VII) (evidence being provided by its U.V. spectrum and colour reactions). The resulting product strongly reduces ammoniacal silver nitrate solution and forms a crystalline 2 : 4-dinitrophenylhydrazone, $C_{23}H_{26}N_6O_4$ (which decomposes above 200° but dose not melt), indicating that an aldehyde group has developed in the product. This is exactly what is demanded by (VI), thus establishing the validity of the structure which is further strengthened by the fact that the base readily develops a tetrahydro-β-carboline nucleus when heated with PCl_5 and Ac_2O and *p*-Tosyl chloride, etc.

In conclusion the author wishes to acknowledge his grateful thanks to Prof. Dr. P. Karrer, Director, Chemisches Institut der Universität Zürich for constructive criticism and to Dr. (Mrs.) Asima Chatterjee, Reader, Pure Chemistry Department, for her helpful suggestions during the progress of this work and also for laboratory facilities.

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DIHYDROTRIAZINES AS POTENTIAL ANTIMALARIALS

By A. Raychaudhuri

Several dihydrotriazines have been prepared from arylamines, possessing either antibacterial or antimalarial activity.

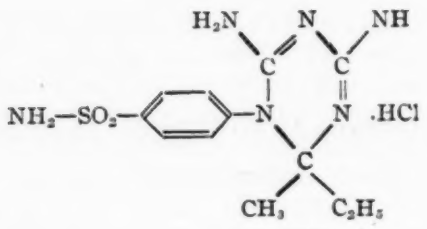
The isolation of a dihydrotriazine as an active metabolite of Paludrine and the search for anticancer compounds led to the synthesis of this new class of compounds with antivitamin and antimalarial activity (Carrington *et al.*, *Nature*, 1951, **168**, 1080; *J. Chem. Soc.*, 1954, 1017; Crowther and Levi, *Brit. J. Pharmacol.*, 1953, **8**, 93; Modest *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 855).

It was thought to be of interest to synthesise some triazines from arylamines possessing either antibacterial or antimalarial activity and to study their pharmacological characteristics. The arylamines used in these syntheses are *p*:*p*′-diaminodiphenyl sulphone and *p*-aminophenylmethyl sulphone, which possess antibacterial activity, and 4-hydroxy-3-diethylaminomethyl-aniline which has some antimalarial action. These arylamines were condensed with dicyandiamide and acetone in presence of hydrochloric acid to afford the corresponding dihydrotriazines as hydrochlorides.

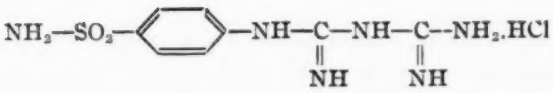
In view of the marked antimalarial activity of 1-*p*-sulphonamidophenyl 2:4-diamino-1:6-dihydro-6:6-dimethyl-1:3:5-triazine hydrochloride (Ray *et al*, *J. Indian Med. Assoc.*, 1954, **24**, 169), an analogous compound (IV) was synthesised from sulphanilamide, dicyandiamide and methylethyl ketone.

Bami (*J. Sci. Ind. Res.*, 1955, **14C**, 231) had attempted to synthesise the above compound (IV), but obtained *p*-sulphonamidophenylbiguanide hydrochloride (V) by the reaction of sulphanilamide, dicyandiamide and aqueous methylethyl ketone Excess of hydrochloric acid in the above reaction led to the formation of *N*-*p*-sulphonamidophenyl-*N*′-guanylurea (VI).

The triazine compound (IV) was prepared in this laboratory by carrying out the reaction with a slight excess of hydrochloric acid and isolated as the hydrochloride. The ultraviolet absorption maximum of this compound in 0.01*N*-HCl was obtained at 244 mμ which was in the region characteristic for triazines of this type (Carrington *et al.*, *loc. cit.*, 1954). The absorption maximum of *N*-*p*-sulphonamidophenyl-*N*′-guanylurea (m.p. 236-38°), prepared by the method of Kundu and Rây (this *Journal*, 1952, **29**, 811), in 0.01*N*-HCl was 255-56 mμ, whereas the absorption maximum of *p*-sulphonamidophenylbiguanide hydrochloride (Basu *et al.*, *Science & Culture*, 1952, **18**, 45) in 0.01*N*-HCl was 266-67 mμ. From the above observations it may be concluded that the compound in question can be definitely taken as a triazine derivative.



(IV)



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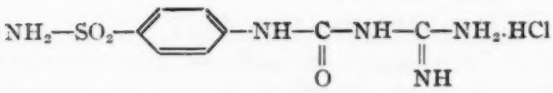

(VI)

Syntheses of a similar type of triazine compounds from sulpha drugs are in progress.

None of the above triazine compounds have shown any significant antimalarial activity when tested against experimental malaria (N.K. Ray, *private communication*).

EXPERIMENTAL

p : p'-*Di*-(2 : 4-*diamino*-1 : 6-*dihydro*-6 : 6-*dimethyl*-1 : 3 : 5-*triazine*-1-*yl*)-*diphenyl Sulphone Dihydrochloride* (I).—*p*:*p*'-Diaminodiphenyl sulphone (1 g.), dicyandiamide (1 g.), acetone (150 c.c.), water (5 c.c.), and HCl (3 c.c.) were kept at room temperature (*ca.* 30°) for 24 hours. The solid separating from the clear solution was collected, washed with acetone, dried and crystallised from aqueous ethanol, m.p. 266-68°. (Found: N, 24·35. $C_{22}H_{28}O_2N_{10}S.2HCl$ requires N, 24.69%). Ultraviolet absorption in 0.01*N*-HCl : λ_{max} 240 mμ. No free amino group was present as evidenced by the diazo test for aromatic amines.

2 : 4-*Diamino*-1-p-*methylsulphonylphenyl*-1 : 6-*dihydro*-6 : 6-*dimethyl*-1 : 3 : 5-*triazine Hydrochloride* (II).—A mixture of *p*-methylsulphonylaniline (5.6 g.), dicyandiamide (2.7 g.), acetone (150 c.c.), HCl (5 c.c.) and water (20 c.c.) was refluxed for 4 hours and left overnight at room temperature. The white crystals were collected and crystallised from aqueous alcohol, m.p. 242°. (Found : N, 20.88. $C_{12}H_{17}O_2N_5S.HCl$ requires N, 21.12%). Ultraviolet absorption in 0.01*N*-HCl : λ_{max} 240 mμ.

2 : 4-*Diamino* 1-(4'-*hydroxy*-3'-*diethylaminomethyl*)-*phenyl*-1:6-*dihydro*-6:6-*dimethyl*-1 : 3 : 5 - *triazine Dihydrochloride* (III). —3-Diethylaminomethyl-4-hydroxyacetanilide (Burckhalter *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 1363) (10 g.) was refluxed for 1 hour with HCl (10 c.c.) and water (10 c.c.). The solution was evaporated to dryness under reduced pressure. The residue was dissolved in absolute alcohol (20 c.c.)

and treated with acetone (400 c.c.) and water (50 c.c.) when a clear solution was formed. Dicyandiamide (2.5 g.) was added to the above solution and refluxed on a water-bath for 16 hours. The solvent was distilled off in vacuo. The viscous residue was triturated with acetone when a pinkish white solid was obtained. This was collected and crystallised from acetone-alcohol mixture, m. p. 196°. (Found: N, 21.2. $C_{16}H_{26}ON_6.2HCl$ requires N, 21.50%). Ultraviolet absorption in 0.01*N*-HCl: λ_{max} 234-36 and 276 mμ.

2 : 4-*Diamino*-1-p-*sulphonamidophenyl*-1 : 6-*dihydro*-6-*methyl*-6-*ethyl*-1 : 3 : 5-*triazine Hydrochloride* (IV).—A mixture of sulphanilamide (2.8 g.), methylethyl ketone (24 c.c.), water (2 c.c.), HCl (1.7 c.c.) and dicyandiamide (1.35 g.) was refluxed on a water-bath for 4 hours and left at room temperature overnight. The crystals were filtered and crystallised from aqueous alcohol, m.p. 210°. (Found: N, 22.22. $C_{12}H_{18}O_2N_6S.HCl$, H_2O requires N, 23.04%). Ultraviolet absorption in 0.01*N*-HCl: λ_{max} 244 mμ.

The author is grateful to Dr. U. P. Basu, D.Sc., F.N.I., Director of the Institute, for his kind interest in the investigation.

BENGAL IMMUNITY RESEARCH INSTITUTE,
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SHORT NOTES

FORMATION OF SILVER^{103} BY BOMBARDMENT OF ENRICHED CADMIUM^{106} WITH PROTONS*

By B. C. Haldar† and Edwin O. Wiig

Neutron-deficient Ag^{103} was previously prepared (Haldar and Wiig, *Phys. Rev.*, 1954, **94**, 1713) by spallation of silver with 80, 100 and 170 Mev protons and identified by milking the Pd^{103} daughter. At lower proton energies a (p, α) reaction on Cd^{106} would be expected to produce Ag^{103}. Since the abundance of Cd^{106} in natural cadmium is only 1.22%, greatly enhanced activity due to Ag^{103} is to be expected on bombarding an enriched Cd^{106} sample.

Enriched Cd^{106} (32.9%)** as CdO and as $CdNH_4PO_4.H_2O$ was bombarded for one hour with protons of 60 and 40 Mev energy in the internal beam of the 130-inch cyclotron of the University of Rochester. Natural cadmium in the form of metal was also bombarded at 60 Mev. The bombarded targets were dissolved in nitric acid, silver carrier was added and silver activity was separated as silver chloride. The latter, after purification by the procedures, used earlier (*loc. cit.*), was counted in a β-proportional counter, a scintillation counter and an X-ray proportional counter.

The silver activity obtained from enriched Cd^{106} targets and measured with the first two counters was found to decay with half lives of 27 minutes and 1.07 hours along with a half life of about 5 hours, the activity of which was less than 1% of the total activity. With the X-ray counter, silver activities of 18 minutes and 1.1 hours were obtained from the CdO target. The silver activity separated from the metallic cadmium target decayed with half lives of 20 minutes, 1.1 hours, 2 6 hours and 5.2 hours, as measured with the β-proportional counter. All the 1.1-hour activities showed the same radiation characteristics as those exhibited by the 1.1 hour Ag^{103} produced earlier (*loc. cit.*). The 27-minute activity is due to Ag^{106}/ or Ag^{104}. The 18 minute activity is probably associated with Ag^{102} which, according to the most recent "Table of Isotopes" (Hollander, Perlman and Seaborg, *Rev. Mod. Phys.*, 1953, **25**, 469), has a half life of 16 minutes.

* This work was supported by the U. S. Atomic Energy Commission.

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Present address: Professor of Inorganic Chemistry and Head of the Chemistry Department, Gujarat College, Ahmedabad.

** Kindly loaned to us by the Isotope Division, Oak Ridge National Laboratory.

The ratio of the Ag^{103} activities obtained at 60 Mev from enriched and normal cadmium, calculated to the end of bombardment and corrected for the difference in target material, was found to be 20 to 1 as compared with an enrichment factor of 27. The cyclotron beam was not monitored but the intensity was approximatety the same. Thus, the 1.1 hour-activity is produced from Cd^{106} and a (p, α) reaction to produce Ag^{103} is suggested.

The authors wish to thank Professor S. W. Barnes, Mr. W. Coombs and the Operating crew of the Rochester 130-inch synchrocyclotron for their assistance with the bombardments.

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QUANTITATIVE ISOLATION OF DL-GLUTAMIC ACID FROM A MIXTURE OF DL-2-PYRROLIDONE-5-CARBOXYLIC ACID AND DL-GLUTAMYLGLUTAMIC ACID

By Seicho Goto, Reiko Goto and Chizuko Goto*

When glutamic acid is isolated from a protein by acid hydrolysis, it is generally assumed that glutamic acid is present in the protein as a straight-chain peptide. During this investigation it is shown that a quantitative yield of DL-glutamic acid is obtained when a mixture of DL-2-pyrrolidone-5-carboxylic acid and the dipeptide DL-glutamylglutamic acid is hydrolysed by hydrochloric acid. This suggests that in a natural protein glutamic acid may be present as a linear peptide as well as a peptide of 2-pyrrolidone-6-carboxylic acid (the cyclic analogue).

A mixture of 129 mg. of DL-2-pyrrolidone-5-carboxylic acid and 276 mg. of DL-glutamylglutamic acid and 25 c.c. of 6*N*-HCl was refluxed on a water-bath for 16 hours. It was then evaporated in vacuum when 541 mg. of a yellowish white crystalline material was obtained. Twice crystallisation of this from distilled water under reduced pressure in a desiccator gave 538 mg. of colorless prismatic crystals, m.p. 196°. (Found: N, 7.56. Calc: N, 7.63%). Its mixed m.p. with a genuine sample of DL-glutamic acid hydrochloride was also 196°. Its R_f value was also identical with that of genuine glutamic acid hydrochloride.

* Contribution from the Research Institute of Science of Goto's Memorial Foundation, No 30, 1-Chome, Sharinjicho, Ikuno, Osaka, Japan.

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STUDIES ON ENZYMES IN THE SYNTHESIS OF NICOTINE ALKALOIDS IN TOBACCO PLANTS

By B. C. Bose, S. S. Gupta and Sultan Mohamed

In a previous communication (Bose *et al.*, *Indian J. Med. Res.*, 1956, **44**, 81), the effect of inorganic nitrogenous sources and various amino-acids on the synthesis of nicotine alkaloids in *Nicotiana tabacum* was reported. It was shown that the different tissues of the tobacco plants possessed capacity to synthesise nicotine from simple substrates like potassium nitrate, ammonium sulphate, tryptophane, proline etc. Klein and Linser (*Planta*, 1933, **20**, 470) and Dawson (*Plant Physiol.*, 1939, **14**, 479), in their feeding experiments with excised tobacco leaves, have also observed nicotine synthesis from various amino-acids. It is therefore of interest to investigate, if alkaloids, like nicotine, could also be synthesised *in vitro* from its precursors or the process can be accelarated with the help of isolated enzyme preparations from tobacco leaves.

The enzymes from leaves, roots and stems of *N. tabacum* and *N. glauca* were extracted by grinding the tissues (10 g.) with 30 c.c. of distilled water at 3° and salting out by cold acetone (5°) after constant stirring. The enzyme, thus precipitated, was dried in vacuo and used for incubation with different substrates in a suitable aqueous medium containing magnesium and sodium sulphates, potassium chloride, calcium dihydrogen phosphate and sucrose in distilled water.

Different concentrations of potassium nitrate (0.1-10 mg.), amino-acids (tryptophane, proline, ornithine, arginine and anthranilic acid), riboflavin and nicotinic acid were incubated as substrates with the enzyme preparations with or without the tissue slices for 24 hours at 37°. The total nicotine synthesised was then distilled off with steam and collected in a receiver containing 5 c.c. of dilute hydrochloric acid. Nicotine content of the distillate was estimated by the cyanogen bromide and aniline colorimetrically, as detailed previously (Bose *et al.*, this *Journal*, 1956, **33**, 131).

From the first sets of experiment, it was observed that potassium nitrate appreciably increased the nicotine content from 0.23μg.–0.36μg., but there was no further enhancement of this synthesis due to addition of isolated enzyme preparations.

As the amino-acids, tryptophane, proline and ornithine, took active part in the *in vitro* synthesis of nicotine by the tissues of tobacco plant (Bose *et al.*, *loc cit.*), a second set of experiments was carried out to investigate whether the isolated enzyme preparations could react with the amino-acid precursors of nicotine synthesis. Incubation of enzyme preparations, isolated from diffrent tissues of tobacco plants, with the substrate medium containing graded doses of amino-acid precursors was, however, found to be ineffective for the synthesis of nicotine alkaloid.

The nicotine synthesis could not be stimulated by adding riboflavin, niacin in the medium containing tryptophane and enzyme extract.

From the different series of investigations, carried out from this laboratory on the biogenesis of nicotine alkaloids, it has been observed that the synthesis of nicotine is accelearated by the addition of amino-acids and inorganic nitrates in *in vitro* as well as *in vivo* experiments. This synthesis, however, is not affected by further addition of isolated enzymes or factors like riboflavin and nicotinic acid.

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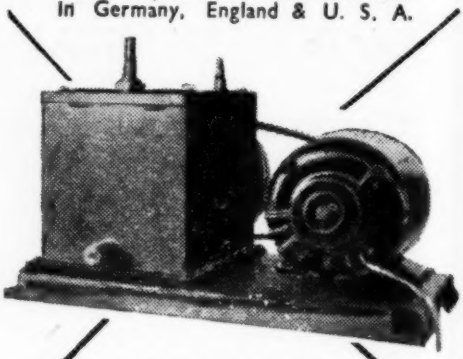

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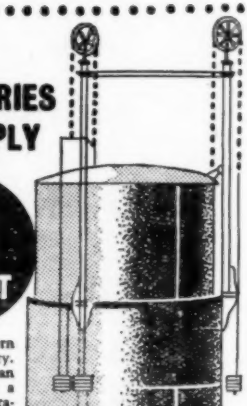

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